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THE STATE OF A SOLID BODY

By E. Grüneisen

Translation of "Zustand des festen Körpers." Handbuch der
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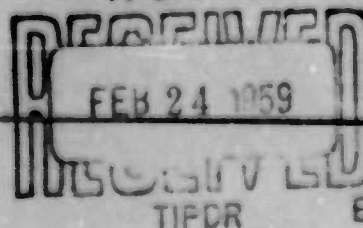
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February 1959

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THE STATE OF A SOLID BODY *

By E. Grüneisen

(a) The Building Up of Solid Bodies

1. Introductory remark. - Since, except for thermal expansion, the properties of solid bodies are treated in the chapter "Heat" and in other parts of this work, we shall, in the following sections, restrict ourselves to a review on the interrelationships of the thermoelastic properties of solid bodies, our aim being to refer these properties back to a few characteristic magnitudes of the atoms, or if possible, to their structure itself. It will be found useful for the presentation to choose the theory of solid bodies whose results, in order to avoid repetition, we will frequently take over from other parts of this work.

2. Definition of a solid body (see ref. 1). - Following the common language usage, the classical theory of elasticity denoted as "solid" any material which offers a continued elastic resistance to any force tending to alter its shape. Thus, glass was just as much a solid body as diamond or metals. From the point of view of the elastic continuum theory, it is even necessary to construe glass as a particularly simple, isotropic, solid material whose properties are independent of the spatial direction. Physical chemistry, on the contrary, denotes a material as solid if it is carried over from the liquid state to the solid state, in the sense of the elasticity theory, through gradual cooling at a sharply defined solidification point with the liberation of a more or less large quantity of heat. Closer investigation shows that material in this state possesses a crystalline structure and therefore possesses in general different properties along different spatial directions; it is anisotropic. Glass has no sharp point of solidification. When cooled down from the liquid state at a higher temperature it becomes increasingly viscous, and the length of time in which it yields to the shape-altering forces becomes increasingly longer; thus while it behaves more and more as a solid body in the sense of the elasticity theory, from the point of view of physical chemistry it is to be regarded as a subcooled liquid. Crystallization is retarded by frictional forces but can occur after a sufficiently long time (devitrification).

* "Zustand des festen Körpers." Handbuch der Phys., Bd. 10, Julius Springer (Berlin), 1926, pp. 1-52.

The molecular theory of solid bodies denotes as solid only those systems of smallest building blocks that are in internal equilibrium, for which therefore each building stone possesses an equilibrium position to which it seeks to return when removed from it. This condition is satisfied, according to our present day view, by homogeneous anisotropic crystals but not by isotropic glass. If, nevertheless, in molecular-theoretical considerations on elastic properties of solid bodies an abstraction is made to the case of isotropic materials, this is done for the sake of simplifying the computations. This case is not strictly realized but is only approximated in the conglomerates of differently orientated small crystallites, such as we usually have, for example, in metals. The smaller the crystallites and the more disordered their orientation, the more is the mass isotropic. A mass of crystallites which has reached a high degree of isotropy, is termed, following W. Voigt, quasi-isotropic. The wide range of mixture crystals, which are rarely in internal equilibrium, and the deformations outside the elasticity limit (plasticity) lie outside the scope of our treatment.

3. The space lattice structure of solid bodies. - Purely crystallographic investigations on the one hand and X-ray analysis of the crystals on the other have given us the knowledge that the building stones of the crystals are arranged in regular space lattices (see, e.g., ref. 2, p. 312ff). With Born (ref. 3) we can think of the most general space lattice as produced in the following manner: From an arbitrary point O let there issue three vectors a , b , and c through which is determined a smallest elementary parallelepiped. Within the latter let there be situated s particles, the building stones of the crystal, which may be partly of the same and partly of a different type. The initial point O , or the lateral surfaces that meet at this point, may likewise contain particles. The totality of the s particles is termed the basis group. The space lattice is now obtained by subjecting the basis group to all translations which are characterized by integral multiples of the vectors a , b , and c . Each of the s particles then gives a simple lattice which consists of only equal particles situated in the points of intersection of three families of parallel, equidistant planes. The most general space lattice thus consists of simple lattices arranged parallel within each other.

Not only the regular lattice arrangement but also the type of the crystal building stones was established through analysis in many cases by means of X-rays. It was found that they are atomic particles which are situated at the lattice points (refs. 2 and 4). Polyatomic solid compounds too can be composed out of simple lattices each of which is occupied by a single type of atom. The conception of the chemical molecule in the solid state thereby loses its significance to a considerable extent, since with the regularity of the atom arrangement in the lattice, it cannot be decided which atom must be ascribed to a molecule. A familiar example of this is rock salt for which a face-centered cubic

sodium lattice is combined with a similar chlorine lattice in such a manner that a simple cubical lattice with regularly alternating sodium and chlorine atoms arises.

Nevertheless, both monatomic and polyatomic space lattices occur such that several atoms of the basis group show a closer connection with each other than with the remaining atoms, as is evidenced in the arrangement itself of the basis group, and as can be shown through physical or chemical properties. Atom groups of this kind within the basis group as a rule embrace those atoms which belong to a chemical molecule or at least to a radical. Familiar examples of such space lattices with group structure are crystals of organic compounds, for example, naphthalene, for which the basis group comprises two molecules, and the carbonates, nitrates, and sulphates of inorganic chemistry in which the radicals CO_3 , NO_3 , and SO_4 essentially independently of the remaining part of the compound form a definite fixed grouping.

It is seen that, in accordance with what was just said, the crystal lattices can be divided into the following types:

- (1) Monatomic lattices without group formation (e.g., diamond and most metals)
- (2) Monatomic lattices with group formation (e.g., sulphur, also bismuth and antimony, although the geometric grouping in four atoms is only weakly pronounced (ref. 2, p. 155))
- (3) Polyatomic lattices without group formation (e.g., the alkali halogen salts)
- (4) Polyatomic lattices with group formation (see the above named examples)

The classification of the crystals in these four categories is often uncertain. The question as to whether a grouping exists has been investigated by a purely geometric method (refs. 5 and 6) but can probably be decided only on the basis of physical properties which give information as to whether the atom group shows within itself a stronger bond than the groups show relative to each other. Only then does the group formation have physical significance.

We have so far not touched upon the question as to what type of atomic particles are to be assumed in the lattice points. Without going more deeply into the structure of these particles here, we can state that the distinction that is made in chemistry between homopolar and heteropolar (or dual) compounds applies also to the crystal lattice. In the case of heteropolar compounds, that is, of a marked salt

character, the lattice points are doubtlessly occupied by ions of alternating sign,¹ that is, by atoms which have given up or taken on one or several electrons, according to whether the atom belongs to an electropositive or an electronegative element. This is proven most clearly through the ability of alternating electrical fields of the frequency of infra red heat rays to excite natural vibrations in such lattices. Lattices whose points are occupied by ions are termed ionic lattices and also atom ion lattices if the ions arose from individual atoms; they are termed radical ion lattices when at least a part of the ions consists of radicals which are bound in the lattice in a solid grouping. Also, radicals such as SO_4 , CO_3 , and NO_3 , as well as the atomic groups of a probably large number of crystals of inorganic and organic compounds, must contain within the group oppositely charged ions, since they possess typical infra red natural vibrations for the corresponding groups (refs. 8 to 12). It is still not known, however, what type of ions are in question here. But the fact remains certain that the radical group as a whole possesses the excess charge which is ascribed to it in the electrolysis, whereas the group forming a molecule is electrically neutral as a whole.

In homopolar monatomic materials ions cannot be detected; the particles occupying the lattice points are apparently electrically neutral atoms. Such lattices are therefore termed atomic lattices. The homopolar organic compounds, since they contain, at most, ions within the molecule but have a homopolar bond between molecules, are termed molecular lattices.

What is the position assumed by the metals from this point of view? The fact that they conduct electricity so much better than nonmetals and that the conduction takes place through moving electrons makes it likely that the metals occupy a middle position between the ionic lattices and the atomic lattices. When the valence electrons at times move far away from the nucleus, as is assumed by Bohr for free metal atoms, they leave an ion behind. If this occurs at the same time for neighboring atoms there is obtained, momentarily and locally limited, a lattice of positive ions with negative electrons dispersed in it. In the next stage these electrons will have approached the nuclei from which they originated or the neighboring nuclei and will build atoms with these. Thus the building stones of the metal space lattices can be denoted now as ions plus electrons, now as atoms.

4. Distribution of the elements and compounds over the different crystal systems. - The division of the crystals into systems and classes is treated in other parts of this work and may therefore be assumed as

¹This idea is first found expressed and justified by E. Madelung in ref. 7. According to him, rock salt, for example, consists of an Na^+ ion lattice and a Cl^- ion lattice.

known. The distribution of the chemical elements and compounds over the different crystal systems will be considered only statistically here. For the elements this can be seen immediately from the adjoining table of the periodic system (table I). For each atom there is given an order number and, as far as is known, the system in which it crystallizes. The abbreviations denote respectively: c, cubic; bc, body-centered; fc, face-centered; hex, hexagonal; tetr, tetragonal; trig, trigonal; rhomb, rhombic; monocl, monoclinic.

It is seen that by far most elements (32) crystallize as regular or cubic crystals, that is, in the system of maximum symmetry; a considerable number (11) are hexagonal, while the less symmetrical systems are only little represented (4 tetragonal, 6 trigonal, 2 rhombic, and 1 monoclinic; elements that occur in different systems are counted each time). Table I teaches us more, however. The crystal structure stands in close relation to the periodicity of the chemical properties and is thus itself approximately a periodic property of the elements. Compare, for example, the occurrence of the hexagonal structure in groups IIb and IVa, the tetragonal in IIIb, and the trigonal in Vb. The elements Si, Ge, and Sn (gray) of group IV follow in their structure the diamond form of carbon by crystallizing regularly in two face-centered cubes which are displaced along the cube diagonally by $1/4$ its length, and so forth. It should also be remarked that systems of lesser symmetry occur only for those elements (except for graphite and γ -manganese) which stand at the end of a period.

This finding favors the supposition that the forces that determine the crystal structure are identical with the valence forces or, as we may say from the viewpoint of Bohr's atom model, that the crystal structure, like the chemical valence of the elements, is determined by the outer structure of the atom.

For compounds, there holds in a corresponding manner the theorem already established by Buys-Ballot (1846) that chemically simple compound substances crystallize in regular or hexagonal crystals. In general, the more complex the composition of the compound, the less the symmetry of the system into which the compound crystallizes; the tetragonal and triclinic systems in particular appear to be uncommon. This is clearly shown by a table set up some time ago by Retgers (ref. 13) which we have corrected as regards the chemical elements (table II). The trigonal system has been included with the computation of the hexagonal.

5. The packing of atoms in the solid state. - A pile of equal spheres which are packed with the maximum possible density has either cubic or hexagonal symmetry; the ratio of the axes of the hexagonal system thus obtained is $c/a = 1.633$. This theorem can easily be proven for models (ref. 14). It seems likely to see in this fact the reason for

the result of the preceding section that by far the greatest number of elements and simplest compounds possess cubic or hexagonal symmetry and that a large part of the hexagonal materials show a ratio of the axes which differs from 1.633 by only a few percent.² We may conclude that for many materials the regular or hexagonal structure is the expression of the fact that each atom stands in the same relation to its neighboring atoms, and thus it is in no way bound more to the one than to the other, and conversely, where the requirements of densest sphere packing are not satisfied the atoms have different relations to their neighbors along different directions.

The conception of rigid spheres which approach each other up to contact can certainly give only a very rough picture of the true arrangement of the atoms in the crystal. It is interesting, however, to follow out a consequence of this conception. According to it the distances of the atoms from their nearest neighbors in the simpler crystal structures must be additively composed of the radii of the "atoms spheres." W. L. Bragg (ref. 15) has tested this law of addition and found it approximately confirmed. He succeeded, by starting, for example, from the distance of the carbon atoms in diamond, in ascribing to the elements constant sphere radii, characteristic for each element, such that through addition of these radii the shortest distances of two atoms in a crystallized element or in a crystallized simple compound can be approximately correctly computed. The relation holds most accurately for the compounds and the electronegative elements, and less accurately for the metals, which in the metallic state give partly larger (up to 20 percent) and partly smaller sphere radii than in the state of the compound. What practical significance a knowledge of these radii can have for the determination of the as yet uncertain crystal structures is shown by F. Rinne (ref. 16) for the example of the cesium halogen salts CsCl, CsBr, and CsI. Assuming that they have the same lattice type as NaCl, the molar volumes computed from the atom sphere radii, known from other considerations, of cesium, chlorine, bromine, and iodine are found to be much larger than when computed from the density and molecular weight, whereas the assumption of a simple cesium cubic lattice space centered within a simple halogen cube lattice gives sufficiently good agreement between both methods of computation (see table III). There can therefore be no doubt that the cesium salts have space centered elementary cubic lattices. This structure was also confirmed with X-rays (ref. 17).

The sphere radii of Bragg show a similar, even more regular, relation to the periodic system of the elements than the atom volumes according to Lothar Meyer. Within each period they decrease from a marked maximum for the alkali metals continuously up to a minimum for the electronegative element at the end of the period and then jump again to the high value of the following alkali metal. We shall not report the numerical values here, since the subject is treated in detail in Volume XXII of this handbook.

²The regular system of densest packing is the surface-centered one.

It may be asked what physical significance is to be ascribed to these Bragg radii or atomic ranges? On the basis of his derivation the radius of the atom or ion in the Bragg sense is that distance from the center of the atom or ion up to which, at usual temperature under the given conditions of the external pressure and the internal forces, another atom can on the average approach. The magnitude of the Bragg atomic volume is thus directly determined only by the extent of the fields of force, not by the extent of the material parts of the atom, whose totality requires a space which could be denoted as a true atomic volume. This would, according to Bohr, embrace the positive nucleus and the electrons, which revolve in groups about the nucleus in more or less extended paths. It is therefore, particularly for the solid state, still insufficiently accurately defined and probably depends on the neighborhood of other atoms (or so-called ionic deformation, see refs. 18 to 20). The Bragg atomic volume and the true atomic volume might therefore be different, and the fact that in many cases they are different was noted by Bragg himself in his cited work. He encounters an apparent contradiction, that the radii of the alkali metal ion according to him are much larger than those of the halogen ion, although according to the Bohr-Kossel theory of atomic structure it must be assumed that, for example, the group of electrons which surrounds the sodium nucleus in rock salt has smaller dimensions than the group of electrons which surrounds the chlorine nucleus. It is striking that the Bragg procedure gives only small differences for the ionic and atomic volumes.

Since, according to the Bohr-Kossel conceptions, the ions are spatially more closed structures than the atoms, it was certainly of advantage, particularly when Fajans, Grimm, and Herzfeld restricted themselves to the ionic volume, to seek to determine first the true radii or volumes for ions. The Bragg procedure is used only for the determination of the difference of the ion radii, namely, for ions which have the same structure type of the outermost electron group, for example, for F^- , Cl^- , Br^- , and I^- , or Na^+ , K^+ , Rb^+ , and Cs^+ , or O^{--} , S^{--} , Se^{--} , and Te^{--} , or Mg^{++} , Ca^{++} , Sr^{++} , and Ba^{++} , and so forth. In the differences of ionic radii thus obtained there is as yet no significant difference as compared with the Bragg numbers (ref. 21). The difference first occurs through new assumptions which must be introduced in order to compute the absolute values of the ionic radii. For the alkali halogen salts these assumptions are the following (ref. 22): (1) The eight outermost electrons of each ion are situated, according to an earlier assumption of Born, at the corner points of a cube, the nucleus resting at its center. The Born-Landé theory (see section 9ff) permits the equilibrium condition to be set up for the attraction and repulsion of the parallel-oriented ion cube in which, in addition to known numbers, only the dimensions of this cube (radii of the circumscribed spheres) and the distance between ions enters. The latter is obtained from experiment. In this way there is obtained for each salt an equation between the two ionic radii of the salt.

(2) It is sufficient, for a salt, for example KCl, to assume the ratio of the radii in order to compute the absolute values for K^+ and Cl^- and, from these, values for all alkali and halogen ions. The ratio of Cl^- to K^+ , with account taken of the requirement of the Bohr-Kossel theory (namely because the nuclear charge of the K^+ ion is larger than that of the Cl^- ion for otherwise equal structure), is chosen somewhat greater than 1 in such manner that the total ionic distances computed from ionic radii of the alkali halogen salts agree best with the observed values. This requirement is satisfied by the ratio $Cl^-:K^+ = 1.2$, that is, a value very different from the Bragg sphere radii ratio $Cl:K = 0.51$.

From similar considerations there are obtained values of the ionic radii for other groups of chemical compounds (ref. 23). For the numerical values reference is made to Volume XXII. The entire method of computing the absolute values of the ionic radii is still quite uncertain. The fact deserves to be mentioned here, however, that for the electronegative ions numerical values are obtained which are not very different from the Bragg sphere radii. Only for the electropositive ions do Fajans, Herzfeld, and Grimm find much smaller dimensions than Bragg, from which follows the important result that according to Fajans and Herzfeld the true volumes of the ions by no means fill out the space of the heteropolar alkali halogen crystal. This result should not, however, be arbitrarily generalized. The space filling will be larger for the atom groups within a crystal which are more solidly bound as radical ions or molecules. It is assumed that in these cases the outer electron orbits of neighboring atoms intermix to a certain extent. Hence, the Bragg radii in this case too will agree approximately with those of the true atom volumes.

That the interspaces of the atoms and ions in metals and in salt crystals cannot be inconsiderable follows also from the phenomena of diffusion and of ion travel in electrolytic conduction in crystals which are made possible through the heat motion of the atoms and ions, and which thus show that the gaps which in the most favorable case occur through the elongations of two neighboring particles are sufficient to permit a third to pass through (see ref. 24 and section 28).

(b) The Forces Acting Between the Atoms

6. General remarks. - Experience teaches that for solid bodies any change of shape or volume, in one sense or another, is opposed by an elastic resistance, or otherwise expressed, the approach or receding of two atoms encounters an elastic resistance. This fact can be most readily understood if the atoms assumed at the crystal lattice points are simultaneously associated with attractive and repulsive forces of which the repulsive forces vary much more rapidly with the increase in distance of the atoms than the attractive forces. Central forces which depend only on the distance of the atoms suggest themselves. In figure 1, K_2

represents the repulsive (negative) force between two atoms which with increasing distance ρ drops very much more rapidly than the attractive (positive) force K_1 . Both forces have the resultant $K_1 - K_2$, that is, a force which for $\rho < \rho_0$ acts negatively or repulses, for $\rho > \rho_0$ acts positively or attracts, but for $\rho = \rho_0$, however, vanishes. At the distance ρ_0 the two atoms are in equilibrium. If the curve drawn for $K_1 - K_2$ were a straight line, the force which drives an atom back to the equilibrium position from which it moved away would evidently be proportional to the distance from the position of equilibrium, and Hooke's law, which constitutes the fundamental assumption of the classical elasticity theory of the continuum, would be satisfied. Actually, the curve for $K_1 - K_2$ according to the assumptions made is without doubt curved, although only over a short interval; that is, for very small changes in the distance of the atoms, it may be considered as rectilinear. Accordingly, a small deformation of a crystal lattice from its equilibrium position will for each individual atom produce a force which is proportional, in the first approximation, to the change in distance from the neighboring atom (quasi-elastic force).

Can we, under this assumption of quasielastic forces for a crystal lattice, derive the well known fundamental equations of classical elasticity theory for a continuum that will represent the totality of the phenomena belonging to the theory of elasticity? This question was already a subject of contention 100 years ago. At that time the molecular elasticity theory failed to gain ground, since it was unable to introduce the required values of elasticity constants into its equations (further information in ref. 3). Thus, for example, according to Poisson, for the simple case of the extended isotropic rod the ratio μ of the transverse contraction to the axial elongation should be $1/4$ independent of the material. Since this was contradicted by tests, the molecular theory appeared condemned. Only much later did Lord Kelvin and recently M. Born show that the molecular theory also gives the correct values of constants if the space lattice of the crystal is built up properly. A simple point lattice (section 3) does not in fact give the full value of the constants, but a space lattice obtained from at least two simple interlaced lattices does, such as we have in the case of the space centered CsCl lattice. Since all known crystal lattices are built up by the interlacing of several simpler lattices, or, as in the case of single atom metals, cannot be construed as simple lattices (ref. 3, second ed., p. 570) because the electrons surrounding the atom nucleus possess a considerable capacity for displacement, the results of the classical elasticity theory can be carried over to the crystal lattice. They lose their validity only where the pointwise distribution of the masses with finite distances of the lattice points has an influence on the phenomena.

The assumption of quasielastic forces does not succeed in explaining the thermal expansion, however, as is readily seen from the simple scheme of figure 1. Let two atoms be in equilibrium at a distance ρ_0 . If one of them is held fixed and the other given an impulse, it will vibrate about the position of equilibrium. If the representing $K_1 - K_2$ curve were a straight line (quasi-elastic force), the atom would carry out pure pendulum oscillations, since the directive force, that is, the quotient of force to elongation, would be constant. The mean distance of the atoms would not change. No grounds would be given for the thermal expansion of the crystal due to the thermal motion of the atoms. If, however, the curve of $K_1 - K_2$ is curved, as in figure 1, the directive force of the atom will decrease with increasing distance from its neighbor, and will increase with decreasing distance; the elongation will be greater when the atom recedes from its neighbor than when it approaches. The mean distance of the atoms increases, and in general there occurs an extension of the solid body as a result of the thermal motion.

As follows from the above, the thermal expansion is intimately related to the variability of the directive force. This force must have, as a consequence, deviations from Hooke's law in that, for example, the extension accelerates and the compression decelerates with an increase in the pressure. Thermal expansion and deviations from Hooke's law are thus intimately related to each other (ref. 25, p. 17).

7. Assumption of forces which vary according to a power of the reciprocal distance. - G. Mie (ref. 26; see also ref. 27, p. 257) in his fundamental work on the kinetic theory of single atom bodies introduced the assumption that both the attraction and repulsion forces between two atoms have a potential which is proportional to a power of reciprocal distance. According to this, the potential energy of two atoms at rest at a distance ρ is given by

$$\varphi = - \frac{a}{\rho^m} + \frac{b}{\rho^n} \quad (1)$$

where the first term refers to the attraction, the second to the repulsion force, and a and b are constants.³ Since $\varphi/2$ represents the potential energy which the one atom has in the neighborhood of the other, there is obtained for the potential energy of the gram atom, in so far as the N atoms in their mean positions corresponding to the temperature are assumed as at rest

$$\Phi = - \frac{a}{2} N \sum \frac{1}{\rho^m} + \frac{b}{2} N \sum \frac{1}{\rho^n}$$

³In fig. 1 of section 6, it is assumed $m = 1$, $n = 3$.

where ρ in the summation denotes the distance from a fixed central atom, that is, sufficiently far from the surface, to the remaining atoms. For the additional potential vibration energy see section 13.

It is of advantage to refer all ρ distances to a fundamental distance r , which, for example, may be so defined that the atomic volume $V = Nr^3$. We then have

$$\Phi = -aN \frac{\sigma_m}{r^m} + bN \frac{\sigma_n}{r^n} \quad (2)$$

where the sums formed for the distances of an atom from all remaining atoms

$$\left. \begin{aligned} \sigma_m &= \frac{1}{2} \sum \left(\frac{r}{\rho} \right)^m \\ \text{and} \\ \sigma_n &= \frac{1}{2} \sum \left(\frac{r}{\rho} \right)^n \end{aligned} \right\} \quad (3)$$

depend only on the spatial arrangement of the atoms, that is, on the crystal structure and on the exponents m and n . The atoms lying near the surface here remain out of consideration (on surface energy see ref. 3, second ed.). Introducing further the atomic volume $V = Nr^3$ we have

$$\left. \begin{aligned} \Phi &= - \frac{A}{V^{m/3}} - \frac{B}{V^{n/3}} \\ A &= aN^{m/3+1} \sigma_m \\ B &= bN^{n/3+1} \sigma_n \end{aligned} \right\} \quad (2a)$$

We remark that A and B may be considered as constants only as long as the σ 's are constant, that is, only if no distortion of the lattice occurs.

Since at the absolute zero point ($T = 0$) and for the external pressure $p = 0$ the atoms are in a position of equilibrium, Φ must have a minimum, from which follows

$$\left. \begin{aligned} \frac{mA\sigma_m}{r_0^m} &= \frac{nB\sigma_n}{r_0^n} \\ \frac{mA}{V_0^{m/3}} &= \frac{nB}{V_0^{n/3}} \end{aligned} \right\} \quad (4)$$

By means of these relations b and B can be expressed through a and A , where r_0 and V_0 , the values of r and V for $p = 0$ and $T = 0$, are to be treated as constants. With these conditions the total potential energy of the gram atom becomes

$$\Phi_0 = -a \frac{N\sigma_m}{r_0^m} \frac{(n-m)}{n} = -\frac{A}{V_0^{m/3}} \frac{(n-m)}{n} \quad (5)$$

In regard to the exponents m and n , it can only be said for the present that $n > m$ (section 6). A second statement in regard to m is obtained through the condition that σ_m must be strongly convergent, that is, the summation over the nearer surroundings of the central atom already gives the value of σ_m with good approximation. For experience teaches that the neighborhood of the surface does not to any large extent influence the energy of an atom in the solid crystal. Therefore, if all atoms are alike and no other force centers exist and also no screening effect of the next neighboring atoms exist, then it is necessary that $m > 3$ (ref. 27, p. 257). Otherwise this restriction can drop out. Mie uses the value $m = 3$; Grüneisen has also considered the case that the effect of distant atoms is screened by the nearest neighbors. The choice of m is then unrestricted. Neither Mie nor Grüneisen have made any assumptions as to the origin of the forces, the power laws being considered only as a working hypothesis in order to bring the thermoelastic properties of single-atom solid material into a theoretical connection. The characteristic constants a , b , m , and n for the atomic forces can thus in the most favorable case be only empirically determined.

8. Heat of sublimation and compressibility of single-atom materials at absolute zero. - Two useful experimental possibilities for determining the constants are obtained without further assumptions. In the first place, the negative contribution of Φ_0 represents the work which is required in order to bring the atoms, assumed unchanged, of a gram atom out of the lattice bond to a large distance from each other. This is, however, the heat of sublimation at absolute zero, which can be approximately determined experimentally.

Secondly, through a simple computation (ref. 28) it is possible to derive the compressibility at absolute zero

$$\kappa_0 = -\frac{1}{V_0} \left(\frac{dV}{dp} \right)_{p=0, T=0}$$

There is obtained (see ref. 27, eqs. (28) and (41), and section 22)

$$\kappa_0 = \frac{9r_0^{m+3}}{m(n-m)\sigma_m a} = \frac{9V_0^{m/3+1}}{m(n-m)A} \quad (6)$$

and by combining with equation (5) the heat of sublimation

$$-\Phi_0 = \frac{9}{mn} \frac{V_0}{x_0} \quad (7)$$

This last equation appears particularly valuable because it permits computing the product of the exponents m and n from observed magnitudes.

9. Electrostatic cohesion in heteropolar lattices. - That the essential cause of cohesion in single-atom solid bodies may be the Coulomb force between atom ions and electrons was first stated by Haber (ref. 29) and supported by computations which have the character of dimensional considerations. He started from the idea that solid material contains a space lattice of electrons in which the atom ions are embedded. With much greater justification than for single-atom materials, whose structural makeup of atoms and electrons is still quite unexplained, Born and Landé (ref. 30) were able to apply the assumption of electrostatic cohesion to the heteropolar two-atom salts after the interlacing of positive and negative ionic lattices first recognized by Madelung for these salts had become a certainty thanks to the X-ray analysis of Bragg. From the Coulomb force action of the valence charges of the ions assumed concentrated at the lattice points, which partly attract and partly repel each other, there results in general a cohesion whose potential energy per mole is obtained from the potential energy of the attraction force in section 7 if we set

$$\left. \begin{aligned} m &= 1 \\ a &= e^2 \end{aligned} \right\} \quad (7a)$$

(e = elementary charge).

The fundamental distance r will again be defined through the relation $V = Nr^3$ where, however, V is now the volume of a mole.

In the sum α_m (eq. (3)) each term further receives as a factor the product of the valences w_z of the central ion and w_k of the k^{th} ion at the distance ρ_k , the valences to be introduced with the sign of the charge, so that

$$\alpha_m = \frac{1}{2} r \sum_k \frac{w_z w_k}{\rho_k} \quad (3a)$$

We thus obtain for the potential energy of the cohesion per mole for $T = 0$, $p = 0$

$$\Phi'_0 = -N\alpha_m \frac{e^2}{r_0}$$

To compute the sums α_m Madelung gave a method which could be utilized by Born and Landé. The fact that in spite of the low exponent $m = 1$ the α_m 's converge rapidly is due to the alternating sign of the members of the series. The α_m (eq. (3a)) have been computed for five lattice types (ref. 3, second ed., p. 746)

NaCl	CaF ₂	ZnS	CsCl	Cu ₂ O
$\alpha_m = 2.2017$	7.3305	9.5324	2.0354	9.5044

For these types the Φ_0 's are then accurately known, since r can be computed from the molecular weight M , density s , and Loschmidt number $N = 6.06 \times 10^{23}$:

$$r = \left(\frac{V}{N} \right)^{1/3} = \left(\frac{M}{sN} \right)^{1/3}$$

10. Electrostatic interpretation of the repulsion force on the basis of the Bohr atom model. - In the above cited work Born and Landé have also given a clarifying reason for the fact that the electrostatic attraction is accompanied by a repulsion which can be set inversely proportional to a high power of the distance between the ions. If, namely, the ions are no longer, as in section 9, regarded as point charges but, corresponding to the ideas of Rutherford, Bohr, and Kossel, as systems with a positive nucleus and revolving electrons, the valence charge appears only as the excess of the nuclear charge over the total charge, or conversely. For at a large distance the charge of the electrons has the same effect as though it were concentrated at the nucleus, the more so the more closely the electron system envelops the nucleus. At short distances, however, the effects of the nucleus and of the electron system must be considered separately. They lead to a potential in the form of a series which starts with $\pm e/\rho$ and progresses with odd powers of $1/\rho$, where ρ is the distance of the external point considered from the ion nucleus. The first term of the series, which essentially comes into question after the Coulomb term, already has a high exponent and corresponds to a repulsion. The value of the exponent of this term depends on the closedness and symmetry of the electron system. Under very simplifying assumptions, namely, neglect of the electron motion, taking account exclusively of the outermost electrons while the inner electrons are ascribed to the nucleus, and assumption of the outermost electrons at the corners of a tetrahedron or cube, we can succeed in computing the exponent n in the potential of the repelling force $+b/\rho^n$. This is, for example, equal to 5 for a tetrahedral arrangement, and equal to 9 for a cubic arrangement with parallel cube surfaces of the neighboring ions. The latter with its eight outer electrons is used by Born for the alkali and halogen ions (outer Li^+) as an approximation (ref. 31).

The magnitude b contains the dimensions of the spheres (ion radii) described about the electron arrangements and is therefore not known. For the potential energy of the repelling forces per mole for $T = 0$, $p = 0$, we have

$$\Phi''_0 = N\sigma_n \frac{b}{r_0^n}$$

and for the total potential energy per mole for $T = 0$, $p = 0$

$$\Phi_0 = \Phi'_0 + \Phi''_0 = -N \left(\frac{\sigma_m e^2}{r_0} - \frac{\sigma_n b}{r_0^n} \right) \quad (3)$$

so that on the basis of equation (4), which now has the form

$$\frac{b\sigma_n}{r_0^n} = \frac{e^2\sigma_m}{nr_0} \quad (4a)$$

we can write

$$\Phi_0 = -N \frac{\sigma_m e^2}{r_0} \left(1 - \frac{1}{n} \right) \quad (8a)$$

11. Lattice energy and compressibility of heteropolar lattices at absolute zero (ref. 3, second ed., p. 733ff). - If n is regarded as known (see above) or computed from the compressibility (eq. (9)) and r_0 is computed from the molar volume, then Φ_0 is fully determined. This is of great significance since $-\Phi_0$ here represents the work which is required to bring the ions from the lattice bond ($p = 0$, $T = 0$) to a large distance (see, however, section 8). This so-called electrostatic lattice energy can also be computed by a quite different method, namely, from the heat of formation of the salt out of the solid metal and gaseous halogen, or from the heat of sublimation of the metal, the ionization energy of the metal, the heat of dissociation of the halogen, and the electroaffinity of the halogen. Both types of computation lead to good agreement, as has been fully discussed in this handbook in Volume XXIV; this supports the assumption that in the simplest heteropolar compounds the electrostatic forces are responsible for holding together the lattice.

A further confirmation of this is obtained by the computation of the compressibility κ_0 from equations (6) and (7a):

$$\kappa_0 = \frac{9r_0^4}{(n-1)\sigma_m e^2} \quad (9)$$

With $n = 9$, the empirical r_0 , and the Madelung values for σ_m , there is obtained for the sodium and potassium halogens as well as for fluorine a value for the compressibility of the correct order of magnitude. If, conversely, the observed values of κ for ordinary temperature are substituted in equation (9) there is obtained

NaCl	NaBr	NaI	KCl	KBr	KI	CaF ₂
$n = 7.84$	8.61	8.45	8.86	9.78	9.31	7.4

The nonconstancy of n can be ascribed to different causes: motion of the electrons, the existence of further terms on the right side of equation (8), and others. That the second named factor plays a considerable part was further justified by Fajans and Herzfeld (ref. 22). By taking into account, in addition to the repulsion term with $n = 9$, further terms with the 5th and 7th power of $1/r_0$ in which the ionic radii similarly enter, they succeeded in setting up an equation corresponding to equation (4a) from which, as described in section 5, they derived values for the ionic radii and then with their aid computed correction terms for Φ_0 . Slater has attempted to extrapolate the κ to $T = 0$ and from κ_0 so obtained to compute n . His values will later be given in table XI.

The lattice energy follows also from equation (7) with $m = 1$.

Schottky (ref. 32; see also ref. 3, second ed., p. 737) has raised against the above derivation of the lattice energy the objection that the ions in the lattice bond and in the gas state are not identical. If the crystal lattice is conceived as a system of electrically charged particles of which the majority, namely the electrons, possess a kinetic energy also at absolute zero and work is expended to gasify the ions at absolute zero, then according to a well known theorem of statistical mechanics, the kinetic energy of the electrons will be reduced by the amount of the expended work, whereby the ions would be altered and in fact enlarged. The lattice energy is therefore not the potential energy between unaltered ions. This is indeed true, although Born has pointed out that in the first place the change in the kinetic energy, that is, the lattice energy, is only small in relation to the total energy content of the ions, and secondly, experience must decide whether the approximate form of the repulsion potential (for only this, and not the Coulomb attraction, changes with the shape of the ions) takes sufficient account of the change of the ions.

Bridgman (ref. 33, p. 165 and especially p. 227ff) too sees in the increase in the kinetic energy, which according to Schottky occurs in the compression of a solid body, a reason for the decrease of the ionic or atomic radii, and thus justification of the atom compressibility, which

had already been surmised by Richards (ref. 34). From this he concludes that the coefficient b in the repulsion potential is not constant. To this may be ascribed the fact that the repulsion exponent n is not only not constant but also often assumes remarkably small values (see table X).

Born (ref. 3, second ed., pp. 696ff and 739) succeeded, for the simplest class of regular lattices (central diagonal lattices) in representing, besides the compressibility, also the elasticity constants c_{11} and $c_{12} = c_{44}$ by a formula in terms of r_0 , m , n , and the elementary charge e .

12. Electrical cohesion in homopolar lattices. - The repulsive forces in homopolar lattices can be explained essentially in the same way as in heteropolar lattices, namely, through the predominating electrostatic repulsion for very close distances of the outermost electrons coupled with the nucleus through quantum laws.⁴ More difficult and as yet quite uncertain are the attempts to explain the cohesion in homopolar lattices through electrical forces. We will here briefly consider only a few of these attempts in which in our opinion an element of the correct situation is contained.

Habor (ref. 36) subsequently took up again the conception of the structure of single-atom metals, which was already mentioned in section 9. The interlaced lattices of monovalent-atom ions and electrons were treated like a heteropolar lattice according to Born and Landé. From the formulas (8a) and (9) and with the aid of auxiliary computations, which need not here be reproduced, values of the repulsion exponent n are obtained of reasonable order of magnitude, for example, copper: 8.0, silver: 9.0, alkali metals: 2.4 to 3.4. There do exist various grounds against the assumption of a fixed electron lattice, particularly in the case of the metals. But even if, as was indicated at the end of section 3, the electron lattice is assumed to have only a temporary locally restricted existence and ion binding effect, Haber's fundamental conception of an essentially electrostatic cohesion will remain a useful one.⁵

⁴See ref. 35, where it is shown how the repulsion force comes about also in the electron motion about the nucleus that is required for the stability of the atom.

⁵See also the related investigations by P. W. Bridgman (ref. 33), who sees the main difficulty in the explanation of the repulsion force between the electron lattice and the ion lattice, and by J. J. Thomson (ref. 37), who does not restrict himself to univalent substances but who fixes a corresponding number of valence electrons corresponding to the valence of the atom in a regular manner within the atom ion lattice and for the entire system computes the potential energy and the compressibility electrostatically.

Landé (ref. 38; see also ref. 39) bases the cohesion of homopolar, and also single-atom crystals, on the assumption that the outer valence electrons of neighboring atoms revolve about their nuclei synchronously, that is, always in the same, or at least a definitely regulated, phase. The fact that attractive forces can arise is made clear by Landé with the aid of the following simple example: Two neutral hydrogen atoms of radius a in a plane, lying near each other at a distance from the nucleus r , give, if the total circular orbits with charge e act uniformly on each other, a repulsion potential of the order $1:r^5$. If, however, the revolving electrons of both atoms have the same phase (fig. 2(a)), the atoms at each instant act on each other like parallel dipoles and in the time average with an attraction potential $-a^2e^2:2r^3$. If there is a counter-motion (fig. 2(b)) of the electrons, then the attraction potential is three times as large. In analogous fashion, in the very much more complicated case of the diamond lattice and under the assumption of a carbon atom model proposed by him, Landé obtains a potential which starts with the term $-\text{Constant} \times r^{-5}$, which is followed by a further attraction term with r^{-7} and a repulsion term with r^{-9} . The lattice constant of diamond is correctly obtained to about 10 percent. The heat of sublimation is obtained as 262 kilocalories per mole in place of the value observed by H. Kohn of 168 kilocalories per mole.⁶ The Landé theory is therefore not quite as it should be, but the fundamental thought of the lattice synchronism probably contains an element of truth and represents a noteworthy attempt to take into account the motion of the electrons. We remark in any case that an attraction potential r^{-3} or r^{-5} for homopolar lattices has in itself nothing improbable about it (section 7).

Still a third possibility of ascribing the cohesion between similar molecules to electrical forces has been described especially by Keesom and Debye (refs. 35, 41, and 42). If such molecules are electrically neutral but still contain electrical dipoles or quadrupoles,⁷ which either exist from before in the molecule or may arise through polarizability (deformability) in the electrical field of the neighboring molecules, then the molecules attract. Keesom and Debye see in this the origin of the Van der Waals cohesion in compressed gases. But forces of this kind may also be assumed as the cause of the holding together of the solid materials, in particular of the molecular lattice, as Born and Kornfeld

⁶According to more recent tests of Kohn and Guckel, the value 147 kcal/mole is considered by Fajans as more probable (ref. 40).

⁷If the center of gravity of the positive electric charges of a model does not agree with that of the negative, then the molecule behaves like a dipole; if all the centers of gravity coincide but the charges possess electrical moments of inertia, then the molecule behaves like an electric quadrupole.

(ref. 43) have attempted to show for the case of the halogen hydrides, whose small heat of sublimation indicates the possibility of this explanation.

All these questions of cohesion, in particular also the question of whether the requirement of chemistry of spatially directed valence forces is sufficiently taken into account by the electrical interpretation of the forces,⁸ are still awaiting further development.

(c) The Energy Content of Solid Bodies

13. The thermal energy of single-atom crystal lattices without group formation. - The potential energy Φ so far discussed of the atoms taken to be at rest at their centers of vibration is only a part of the total energy content of solid bodies. A further part is formed by the thermal energy E , that is, by the energy of the vibrations which are carried out by the lattice building stones about their positions of rest. Accordingly, the total energy content of a mole of the solid body at the temperature T is

$$U = \Phi + E \quad (10)$$

where E is given by the energy increase gained by the mole if it is heated from absolute zero at constant volume up to the temperature T . Whether the volume V_0 or V_T is here held constant makes little difference. We set

$$E = \int_0^T C_V dT \quad (11)$$

As was already indicated in section 6, the directive force of the atom under the influence of the neighboring atom cannot be constant because no thermal expansion would otherwise be obtained. In spite of this, at not too high temperatures, as long as the change of the directive force with the amplitude is not appreciable, the mean kinetic energy may be set equal to the mean potential energy of the atoms referred to their vibration centers for every pure sine vibration; E is therefore, with the given restrictions, half kinetic and half potential energy. On this is based the justification of the Dulong-Petit law given by Boltzmann (ref. 45) and later by Richarz (ref. 46). For under the assumption of the law of equipartition of the energy, E would for the gram atom of a monatomic solid body have to be twice as large as the mean kinetic energy

⁸This is doubted in particular by W. Nernst in ref. 44; on the other hand, see ref. 20.

of a gram atom in the ideal gas state, that is, $E = 2 \times 3RT/2 = 3RT$; $C_v = 3R = 5.96$ cal/deg. The fact that experiment has given the constancy of the atomic heat at most for a restricted temperature range but toward the lower temperatures a strong decrease up to vanishing in the neighborhood of absolute zero (ref. 47), and that this behavior can be largely explained if, instead of the equipartition law of the energy, the quantum theory is used as a basis will be presented in detail in other parts of this work. Here we can only briefly repeat those results which are essential for what follows.

The starting point of the newer theory of specific heats was given by Einstein's formula for a monochromatically vibrating gram atom

$$\left. \begin{aligned} E &= 3RTP \left(\frac{\theta}{T} \right) \\ P(x) &= \frac{x}{e^x - 1} \end{aligned} \right\} \quad (12)$$

where θ is connected with the frequency ν of the atom and with Planck's constant h , and $k = R/N$ through the relation $\theta = h\nu/k$ and denotes a characteristic temperature for the change of the energy content of the solid body under consideration. For the atomic heat there follows from equation (12)

$$\left. \begin{aligned} C_v &= 3RH \left(\frac{\theta}{T} \right) \\ H(x) &= \frac{x^2 e^x}{(e^x - 1)^2} \end{aligned} \right\} \quad (12a)$$

that is, a function which starting from the value 0 for $T = 0$ rises to the limiting value $3R$ for large T the more slowly the higher the frequency ν or the characteristic temperature θ . Although the Einstein formula has proven itself fruitful in so far as the drop of the atomic heat of monatomic solid bodies according to a universal function of θ/T was sufficiently well confirmed, the form of the function $H(x)$ was still in no way sufficient.

A very satisfactory approximation to the experimental results was attained by Debye⁹ by his assuming that the heat vibrations are not monochromatic but embrace the total region of the possible elastic vibrations in the body. He obtained for the vibration energy of the gram atom of a

⁹The computation of the functions $D(x)$ and $C(x)$ is given in refs. 47 and 48.

monatomic isotropic material the formulas

$$\left. \begin{aligned} E &= 3RTD\left(\frac{\theta}{T}\right) \\ D(x) &= \frac{3}{x^3} \int_0^x \frac{\xi^3}{e^\xi - 1} d\xi \end{aligned} \right\} \quad (13)$$

and for the atomic heat

$$\left. \begin{aligned} C_V &= 3RC\left(\frac{\theta}{T}\right) \\ C(x) &= \frac{12}{x^3} \int_0^x \frac{\xi^3}{e^\xi - 1} d\xi - \frac{3x}{e^x - 1} \end{aligned} \right\} \quad (13a)$$

where now the frequency ν , which multiplied by h/k gives the characteristic temperature θ of the material, denotes an upper limit of the elastic vibration spectrum whose existence can readily be seen as necessary. It will be attained when neighboring atoms vibrate with a relative phase shift of 180° . By assuming that even for this maximum limiting frequency the same velocity of elastic waves holds as for slow acoustic vibrations and by further introducing only a mean velocity of sound \bar{u} which is connected with the velocities for longitudinal waves u_l and transverse waves u_t through the relation

$$\frac{1}{\bar{u}^3} = \frac{1}{3} \left[2 \frac{1}{u_l^3} + \frac{1}{u_t^3} \right]$$

Debye obtained the simple relation

$$\theta = \frac{h}{k} \bar{u} \sqrt[3]{\frac{3N}{4\pi V}} \quad (14)$$

through which therefore the characteristic temperature or limiting frequency of the atom vibrations can be computed from the elastic properties of the material.

Particularly simple, according to Debye, is the curve of the atomic heat at very low temperature. If $T < \theta/12$, then with less than 1 percent error

$$\left. \begin{aligned} E &= \frac{3\pi^4}{5} \frac{R}{\theta^3} T^4 \\ C_V &= \frac{12\pi^4}{5} \frac{R}{\theta^3} T^3 \end{aligned} \right\} \quad (15)$$

The equations (13), (13a), and (15) have been well confirmed by Nernst and his coworkers for single-atom regularly crystallizing materials; the validity of equation (14) is less certain (see below).

The more strict Born (ref. 3, second ed., p. 645ff., and ref. 49) formulation of the theory of the atomic heat for single-atom crystal lattices without group formation (section 3) separates the longitudinal and transverse elastic waves and takes into account the change of their velocities with the direction in the crystal. It gives, after integration over the solid angle Ω :

$$\left. \begin{aligned} E &= RT \sum_{j=1}^3 \int_0^{\left(\frac{\theta_j}{T}\right)} \frac{d\Omega}{4\pi} \\ C_V &= R \sum_{j=1}^3 \int_0^{\left(\frac{\theta_j}{T}\right)} \frac{d\Omega}{4\pi} \end{aligned} \right\} \quad (16)$$

but takes over for θ_j as a first approximation the Debye formula

$$\theta_j = \frac{h}{k} u_j \sqrt[3]{\frac{3N}{4\pi V}} \quad (14a)$$

where j denotes the type of wave, and θ and u depend further on the direction. Here also no account has been taken of a change of the sound velocities with the wave length (elastic dispersion) wherein there appears to be a further deficiency of equation (14a) particularly in the application to nonregular monatomic crystals for which equations (16) should otherwise hold (ref. 50).

The limiting laws (15) also according to Born and von Kármán remain valid at low temperatures if θ is to be understood as a suitable mean value. At higher temperatures, however, the atomic heat is not necessarily representable through the same or even through a single θ value.

14. The thermal energy of the other crystal lattices. - Polyatomic lattices without group formation obey the same laws as the single-atom lattices just discussed if the masses of the compound components are nearly equal to each other (e.g., KCl). This has been established experimentally by Nernst and his coworkers and is also understandable theoretically. If, on the contrary, the masses are very different, then the elastic spectrum does not form a single region of "acoustic" vibrations closed off by the limiting frequency, but it possesses in addition more or less separated spectral branches of higher frequency that may as a first approximation be treated as monochromatic (ref. 49) whose number for a p -atom lattice is at most $3(p - 1)$.

A similar consideration holds for the lattices with group formation whether they are one-atom (as for sulphur) or many-atom lattices. For these it has already been shown by Nernst that within the fast-bound groups it is equally necessary to assume monochromatic vibrations whose energy contribution may be given by equation (12). The same formal result is arrived at by the Born theory of many-atom lattices (ref. 3, second ed., p. 646), according to which the thermal energy of a p-atom body per mole may be approximately represented by

$$E = RT \left\{ \sum_{j=1}^3 \int D\left(\frac{\theta_j}{T}\right) \frac{d\Omega}{4\pi} + \sum_{j=4}^{3p} P\left(\frac{\theta_j}{T}\right) \right\} \quad (17)$$

and the molar heat may be represented by

$$C_V = R \left\{ \sum_{j=1}^3 \int C\left(\frac{\theta_j}{T}\right) \frac{d\Omega}{4\pi} + \sum_{j=4}^{3p} H\left(\frac{\theta_j}{T}\right) \right\} \quad (17a)$$

The terms which are characterized by $j = 1$ to 3 refer to the contributions of the longitudinal and two transverse vibration spectra; their θ_j 's depend on the direction in the crystal; the terms characterized by $j = 4$ to $3p$ are the contributions of the more or less monochromatically acting inner vibrations, which may under certain conditions be observed through the metallic reflection in the infrared region (residual rays).

15. The thermal energy at high temperature. - The formulas of the foregoing sections assume that the atoms vibrate quasi elastically, as is the case only for small vibration amplitudes, that is, at low temperature. For larger amplitudes Hooke's law no longer holds (section 6), and therefore the atomic heat, for example, of a single-atom solid body at high temperature must rise above the limiting value $3R = 5.96$ cal that follows from equation (13a) or (16). This had been pointed out much earlier by Richarz (ref. 46). Born and Brody (ref. 51 see also ref. 52) computed the effect of the anharmonic character of the vibrations and obtained for the atomic heat of a single-atom solid body at high temperature

$$C_V = 3R[1 - \sigma 3RT]$$

σ is also theoretically obtained as probably negative. The atomic heat C_V therefore increases linearly with T and in such a manner as though this increase is maintained from the value $3R$ on. The testing of platinum and copper appears to confirm this formula (refs. 24 and 53). For more details see the article by Schrödinger in this volume.

(d) The Changes of State of Solid Bodies

16. Free energy and entropy of solid bodies. - All questions which concern the changes of state of solid bodies can in principle be answered if one of the characteristic functions, which is denoted as free energy or entropy, is known. We shall start from the free energy and chose as our starting point again the following formula from the Planck theory for the free energy of a resonator (see, e.g., ref. 54)

$$j = kTF\left(\frac{\theta}{T}\right)$$

where

$$F(x) = \ln[1 - e^{-x}]$$

From this there is obtained the free energy of a monochromatically vibrating gram atom (ref. 55) of a single-atom solid body

$$F = \Phi + 3RTF\left(\frac{\theta}{T}\right) \quad (18)$$

The potential energy Φ of the atoms considered as at rest at their vibration centers is for constant volume independent of T . Accordingly, there is obtained for the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3R\left[P\left(\frac{\theta}{T}\right) - F\left(\frac{\theta}{T}\right)\right] \quad (19)$$

The assumption of monochromatic vibrations holds true with a certain approximation, as we saw, only for the internal vibrations of atom groups. For the heat motion of the atoms, however, it is necessary according to Debye (ref. 25, p. 29) to take into account the total elastic frequency spectrum, and for the assumption of the isotropy and a single mean θ (corresponding to the Debye limiting frequency) there is obtained for the free energy of the single-atom solid body

$$\left. \begin{aligned} F &= \Phi + 3RT \left[3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} F(x)x^2 dx \right] \\ &= \Phi + 3RT \left[F\left(\frac{\theta}{T}\right) - \frac{1}{3} D\left(\frac{\theta}{T}\right) \right] \end{aligned} \right\} \quad (20)$$

and for the entropy of the single-atom isotropic solid body

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3R\left[\frac{4}{3} D\left(\frac{\theta}{T}\right) - F\left(\frac{\theta}{T}\right)\right] \quad (21)$$

The entropy is thus here too a function of θ/T .

In the general case of a p-atom solid body whose thermal energy can not be given by a limiting frequency (θ) but, according to equation (16) or (17), the free energy according to Born (ref. 3, second ed., eq. (317), p. 678) has to be combined from equations (18) and (20) and a mean space value must be formed over F and D in equation (20) whereby there is obtained the following expression, which however is only approximately valid: The free energy of an arbitrary crystal lattice whose smallest cell out of which the lattice can be built up contains p atoms is per mole

$$F = \Phi + RT \sum_{j=1}^3 \int \left[F\left(\frac{\theta_j}{T}\right) - \frac{1}{3} D\left(\frac{\theta_j}{T}\right) \right] \frac{d\Omega}{4\pi} + RT \sum_{j=4}^{3p} F\left(\frac{\theta_j}{T}\right) \quad (22)$$

The entropy in this case is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = R \sum_{j=1}^3 \int \left[\frac{4}{3} D\left(\frac{\theta_j}{T}\right) - F\left(\frac{\theta_j}{T}\right) \right] \frac{d\Omega}{4\pi} + R \sum_{j=4}^{3p} \left[P\left(\frac{\theta_j}{T}\right) - F\left(\frac{\theta_j}{T}\right) \right] \quad (23)$$

17. The equations of state of solid bodies. - For a monatomic isotropic solid body there is obtained the usual equation of state from equation (20) according to the known thermodynamic relation

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

as the equation

$$p = -\left(\frac{\partial \Phi}{\partial V}\right)_T - \frac{1}{\theta} \left(\frac{\partial \theta}{\partial V}\right)_T 3RT D\left(\frac{\theta}{T}\right) \quad (24)$$

or without account taken of equation (13)

$$\left(p + \frac{\partial \Phi}{\partial V}\right) V = - \frac{\partial \log \theta}{\partial \log V} E \quad (24a)$$

If E denotes any function of θ/T and not the special Debye form, then equation (24a) is essentially identical with that of Mie (ref. 26, eq. (28)) and Grüneisen (ref. 56) from the virial law and under the assumption of exponential force laws for Φ (see eqs. (2) and (2a)). The interpretation of the multiplier of E as the negative ratio of the relative changes of the atomic frequency and of the volume was given by Grüneisen. The derivation of the equation from the entropy is due to Ratnowsky (ref. 57), from the free energy to Debye (ref. 25, p. 17).

The equation of state (24a) holds for arbitrary forms of Φ and E provided E is determined by a single characteristic frequency. It may therefore be regarded as valid also for single-atom regular crystals without group formation if its atomic heat can be represented by the Debye equation (13a).

In order to be able to take into account also changes in state that are connected with change in shape, it is necessary to take Φ as a quadratic form of the six deformation components $x_x, y_y, z_z, y_z, z_x,$ and x_y and also regard θ as dependent on these and to use the relations

$$x_x = - \frac{\partial(F/V)}{\partial x_x}, \quad y_y = - \frac{\partial(F/V)}{\partial y_y}, \quad \dots$$

$$y_z = - \frac{\partial(F/V)}{\partial y_z}, \quad \dots$$

In this way there are obtained from equation (20) six equations of state (ref. 25, p. 17, and refs. 58 and 59, p. 549)

$$x_x = - \frac{\partial(\Phi/V)}{\partial x_x} - \frac{\partial \log \theta}{\partial x_x} \frac{E}{V} \quad (25)$$

The equations of state immediately lose their simplicity and clearness if we go over to the case of an arbitrary crystal lattice whose free energy per mole is given by equation (22). There is then obtained in place of equation (25)

$$x_x = - \frac{\partial(\Phi/V)}{\partial x_x} - \frac{RT}{V} \sum_{j=1}^3 \int \frac{\partial \log \theta_j}{\partial x_x} D\left(\frac{\theta_j}{T}\right) \frac{d\Omega}{4\pi} - \frac{RT}{V} \sum_{j=4}^{3p} \frac{\partial \log \theta_j}{\partial x_x} P\left(\frac{\theta_j}{T}\right) \quad (26)$$

It is seen that these equations can go over into the simple form of equations (25) only if the factors $\partial \log \theta_j / \partial x_x$ have a constant value independent of the direction in the crystal and the type of vibration, for this constant value then occurs before the space integrals and summations \sum as a common factor of E/V (see eq. (17)). In general, however, those factors will be different for different directions and types of vibration.

18. Variability of the atomic frequencies in deformations. Frequency formula of Madelung-Einstein. - From the form of the equations of state of solid bodies it is clear what an important role in the changes of state is played by the variability of the atomic frequencies

in the deformation of the solid body. We must try to obtain information on this variability. As far as concerns the limiting frequencies of the elastic spectrum it might be supposed that the question as to the variability of θ' or θ_j is answered in equations (14) and (14a). This, however, is not the case, because these equations have Hooke's law as their basic assumption, and it is precisely the variability of the elastic constants in a deformation, that is, the deviations from Hooke's law, that is here in question.

The possibility of taking into account these deviations is given by the assumption of the exponential law for the atomic forces (sections 7 to 12). While referring to Born's atomic theory of the solid state (ref. 60, p. 674ff) for a stricter presentation we shall be satisfied here with deriving a rather rough, as regards the absolute value, but as regards the effect of a change of volume a sufficiently accurate, computation of the limiting frequency of a single-atom solid body from the laws (ref. 56).

Let it be assumed that all atoms except one are held fixed. This single atom is displaced from its position of rest by an amount ζ , whereby the potential energy $D\zeta^2/2$ results (D = directive force). If μ is the mass of the atom, then under the effect of the remaining atoms it can carry out vibrations with the frequency

$$\nu = \frac{1}{2\pi} \sqrt{\frac{D}{\mu}}$$

According to the power laws of section 7 the force between two atoms at a distance ρ is

$$f(\rho) = -\frac{ma}{\rho^{m+1}} + \frac{nb}{\rho^{n+1}}$$

If N_p is the number of atoms of a regular lattice at the distance ρ_p from the vibrating atom and δ_p the angle which the connecting line to the vibrating atom makes with the direction of the vibration ζ , the retarding force is

$$-D\zeta = \sum_p \left\{ f(\rho_p + \zeta) - f(\rho_p - \zeta) \right\} N_p \cos^2 \delta_p$$

or approximately

$$-D\zeta = 2\zeta \sum_p f'(\rho_p) N_p \cos^2 \delta_p$$

if the summation is extended over the atoms of a half-space. Summing over the entire space and introducing the value of $f(\rho)$ and the fundamental distance $r = \sqrt[3]{V/N}$ there is obtained

$$D = - \frac{m(m+1)}{r^{m+2}} a s_m + \frac{n(n+1)}{r^{n+2}} b s_n$$

where s_m is defined in correspondence with s_n and

$$s_n = \sum_p \left(\frac{r}{\rho_p} \right)^{n+2} N_p \cos^2 \delta_p$$

depends only on n and the lattice structure of the solid body. Eliminating b by means of equation (4) and setting, with account taken of equation (3),

$$\psi_n = \frac{s_n}{\sigma_n} = \frac{\sum_p \left(\frac{r}{\rho_p} \right)^{n+2} N_p \cos^2 \delta_p}{\frac{1}{2} \sum_p \left(\frac{r}{\rho_p} \right)^n} \quad (27)$$

there is finally obtained

$$v^2 = \frac{1}{4\pi^2} \frac{D}{\mu} = - \frac{ma\sigma_m}{4\pi^2 \mu r^{m+2}} \left\{ (n+1) \psi_n \left(\frac{r_0}{r} \right)^{n-m} - (m+1) \psi_m \right\} \quad (28)$$

Making use of equation (6) we can write

$$v^2 = \frac{9r_0}{4\pi^2 (n-m) \mu x_0} \left\{ (n+1) \psi_n \left(\frac{r_0}{r} \right)^{n+2} - (m+1) \psi_m \left(\frac{r_0}{r} \right)^{m+2} \right\} \quad (29)$$

In this way the atomic frequency is again brought in relation with the elastic properties of the material, in this case, however, only with the limiting value of the compressibility for $T = 0$, $p = 0$, whereas Debye's formula (14) contains the sound velocities and hence also the remaining elasticity constants (in the case of isotropic material, therefore, also the ratio of the transverse contraction to the longitudinal elongation).

Introducing further the atomic volume $V = Nr^3$ and the atomic weight $M = N\mu$, equation (29) can be written

$$v^2 = z^2 N^{2/3} \frac{v_0^{1/3}}{M x_0} \quad (29a)$$

where the numerical factor

$$z^2 = \frac{9}{4\pi^2} \frac{(n+1)\psi_n \left(\frac{V_0}{V}\right)^{\frac{n+2}{3}} - (m+1)\psi_m \left(\frac{V_0}{V}\right)^{\frac{m+2}{3}}}{n-m} \quad (30)$$

is in any case of the order of magnitude 1 but varies with the volume ratio V/V_0 .

The assumption of the power law influences only the factor z^2 . Except for this, equation (29a) is identical with the formula first set up by Madelung (refs. 7 and 60; see also ref. 61) for halogen salt lattices and later by Einstein (ref. 62) for single-atom substances which may be employed for the computation of the limiting frequency for the representation of the observed atomic heats if there is set $z^2 = 0.13$.

As regards the values of the magnitudes ψ_m and ψ_n , which are defined by equation (27), the summations in the numerator and denominator for large n can be broken off after taking account of the nearest neighboring atom so that ψ_n becomes independent of n . With decreasing exponent, however, the atoms at a further distance must be taken into account, particularly in the denominator of ψ , whereby the latter becomes considerably larger than the numerator. In the case $m \sim 3$ observed by Mie and Grüneisen, which according to section 12 can probably be theoretically justified for homopolar materials, we have $a_m \gg s_m$, $\psi_m \ll \psi_n$, so that

$$v^2 = \frac{9(n+1)\psi_n r_0}{4\pi^2(n-m)\mu x_0} \left(\frac{r_0}{r}\right)^{n+2} = \frac{9(n+1)\psi_n}{4\pi^2(n-m)} \frac{N^{2/3} V_0^{1/3}}{M x_0} \left(\frac{V_0}{V}\right)^{\frac{n+2}{3}} \quad (29b)$$

Under the above mentioned assumption $\psi_m \ll \psi_n$, which holds also for the simplest regular ionic lattice without group formation, the relative change of the limiting frequency v or of the characteristic temperature $\theta = hv/k$ with the atomic distance or volume is therefore given by

$$\left. \begin{aligned} -\frac{d \log v}{d \log r} &= -\frac{d \log \theta}{d \log r} = \frac{n+2}{2} \\ -\frac{d \log v}{d \log V} &= -\frac{d \log \theta}{d \log V} = \gamma = \frac{n+2}{6} \end{aligned} \right\} \quad (31)$$

The relative change in frequency is therefore a low multiple of the change in volume, the numerical factor γ standing in a simple relation

to the exponent of the repulsion force. The factor γ is of the order of magnitude 1 and under the assumptions made is a constant for each material. Materials with equal repulsion exponents have the same value of γ .

If the assumption $\psi_m \ll \psi_n$ is not introduced, there is obtained more generally from equation (29a)¹⁰

$$-\frac{d \ln v}{d \ln V} = \gamma = \frac{1}{6} \frac{(n+1)(n+2)\psi_n - (m+1)(m+2)\psi_m}{(n+1)\psi_n - (m+1)\psi_m} \quad (32)$$

It is easily seen that for fixed n in the case of the neglecting of ψ_m the value of γ comes out smaller than when ψ_m has any appreciable contributions. For in the numerator of equation (32) the second term in relation to the first is smaller than in the denominator. The denominator decreases relatively more strongly than the numerator; γ increases with increasing effect of the structural factor ψ_m . In the limiting case $\psi_m = \psi_n$ the relation is obtained

$$\gamma = \frac{m+n+3}{6} \quad (33)$$

In general θ depends not only on the volume but on all six deformation components $x_x, y_y, z_z, y_z = z_y, z_x = x_z$, and $x_y = y_x$, through which an arbitrary deformation can be described. To the magnitude $\gamma = -d \log \theta / d \log V$ correspond the partial differential coefficients

$$\gamma_{xx} = -\frac{\partial \log \theta}{\partial x_x}, \gamma_{yy} = -\frac{\partial \log \theta}{\partial y_y}, \dots, \gamma_{xy} = -\frac{\partial \log \theta}{\partial x_y} \quad (34)$$

These coefficients are in general different for each type of vibration and for the elastic frequency spectrum depend on the direction of the wave in the crystal. Little can be said theoretically regarding their numerical values (ref. 25, p. 40).

For regular single-atom lattices for which a single θ is generally sufficient, the equations hold

$$\gamma_{xx} = \gamma_{yy} = \gamma_{zz} = \gamma$$

¹⁰Ref. 56, p. 269, eq. (11a). A more strict computation of the magnitude γ for centered diagonal lattices is given by Born (ref. 3, second ed., p. 691ff).

since for a volume change ($y_z = z_x = x_y = 0$) we have

$$-\frac{\Delta\theta}{\theta} = \gamma_{xx}x_x + \gamma_{yy}y_y + \gamma_{zz}z_z = \gamma \frac{\Delta V}{V} = \gamma(x_x + y_y + z_z)$$

For regular ionic lattices without group formation, several θ_j 's for the thermal energy will in general be required, but it will be possible similarly to assume as an approximation that

$$(\gamma_j)_{xx} = (\gamma_j)_{yy} = (\gamma_j)_{zz} = \gamma_j \quad (35)$$

and that all γ_j 's ($j = 1, 2, \dots, 3p$) are equal to each other.

For nonregular lattices without group formation γ_{xx} , γ_{yy} , and γ_{zz} are in general different but still of equal order of magnitude.

If a lattice has atom groups which in themselves are more strongly coupled than the groups with each other, then through a volume change or other deformations the distances of the atoms within the groups are less strongly changed than the distances of the centers of gravity of the groups, between which relatively weak forces are effective. Hence also the high frequencies, which are based on the strong coupling within the groups and to which correspond the θ_j 's ($j = 4, \dots, 3p$) of equations (17) and (17a), will certainly be less influenced than the relatively low Debye limiting frequencies of the elastic spectrum, for which the loose coupling between the groups is the determining factor. We may therefore, depending on the type of the vibrations, have to deal with quite different values of γ . If we disregard the differences in the three directions x , y , and z , then we must suppose that the γ_j 's ($j = 4, \dots, 3p$) may be considerably smaller than the γ_j 's ($j = 1, 2, 3$), the more so the stronger the coupling within the groups, and that the γ_j 's ($j = 1, 2, 3$) must have about the same magnitudes as the γ 's for regular single-atom lattices without group formation.

The foregoing considerations are, it is true, only of a qualitative kind and still lack a solid foundation, but they will be useful to us in the interpretation of the consequences of the equations of state.

19. Equation of state for isotropic or regularly crystallizing single-atom solid bodies for the assumption of the power force law. - From equation (24a), after introducing the value of ϕ from equation (2a) and the value for $-d \log \theta / d \log V$ from equation (31), there follows the equation of state

$$\left[p + \frac{m}{3} \frac{A}{v^{\frac{m}{3}+1}} - \frac{n}{3} \frac{B}{v^{\frac{n}{3}+1}} \right] v = \frac{n+2}{6} E \quad (36)$$

Setting $E = 3RT$ and $m = 3$, we have the Mie equation of state. In place of equation (36) we may write in the abbreviated form

$$pV + G(V) = rE \quad (37)$$

where

$$G(V) = \frac{m}{3} \frac{A}{V^{m/3}} - \frac{n}{3} \frac{B}{V^{n/3}} \quad (38)$$

In agreement with equation (4) therefore, for $p = 0$ and $T = 0$, we have

$$G(V_0) = 0 \quad (38a)$$

20. Change of state at constant volume. Single-atom regular crystals. - If we heat a solid body whose thermal energy E can be represented by a single characteristic temperature θ , at constant volume, then, regardless of what special form Φ may have, there holds, according to equation (24a), the relation

$$\left(\frac{\partial p}{\partial T}\right)_V V = rC_V$$

or, with account taken of a known thermodynamic relation,

$$-\frac{V\left(\frac{\partial V}{\partial T}\right)_P}{C_V\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{V\left(\frac{\partial V}{\partial T}\right)_P}{C_P\left(\frac{\partial V}{\partial P}\right)_S} = \gamma \quad (39)$$

where the subscript S denotes the adiabatic change of state. On the left side of equation (39) are purely observable magnitudes, atomic volumes, the thermal expansion coefficient, the atomic heat, and compressibility, from which the important magnitude γ can be computed.

Table IV gives the values of γ for all regularly crystallizing elements for which the magnitudes in question are known (see the first columns of the table). Manganese is thus included, although it is said to occur in three modifications (ref. 70), of which two form a complicated cubic system and the third belongs to the tetragonal system, and it is doubtful to which modification the observations of the table refer.

In the last column of table IV, there have also been computed, under the assumption that equation (31) is valid, the exponents $n = 6\gamma - 2$.

Since no assumption has been made on the value of m , neither the picture of neutral atoms at the lattice points, between which forces of an as yet unknown type exert an attraction, nor Haber's picture of interlaced atomic ions and electrons, and so forth, needs to be applied.

The values of γ and n are, as the theory requires, of the same order of magnitude for the different elements, a fact which, in view of the different compressibilities in the ratio 1:400, is very noteworthy. While they deviate to some extent from one element to the next, the fluctuations are not accidental but show certain regularities which are best recognized if the elements possessing equal crystal structure are collected. Table V (a) gives the space-centered elements and V (b) the face-centered cubic elements.¹¹ Their sequence corresponds to their atomic number except that the alkali metals are placed ahead as a group by themselves. It is seen that the alkali metals have the smallest γ 's and n 's; the remaining space-centered elements have clearly larger values, and within each group an appreciable constancy is observed. The face-centered elements have still larger values of γ and n , which on the whole increase with increasing atomic number. Diamond, with its special structure, and phosphorus would fit into the group of the alkali metals, and manganese into the group of the face-centered cubic elements.

As previously indicated (section 10), values of n between 5 and 9 have been theoretically derived by Born and Landé for certain special cases of electrostatically repelling electron systems. An increase of the n value above 9 can be ascribed either to electron systems which very closely envelop the atom nucleus, as in the case of the heavy atoms, or to the fact that the application of equation (31) to the computation of n is inadmissible and that equation (32) must be used instead. According to the latter, smaller values of n will be obtained from the values of γ , in the limiting case (eq. (33)) by $m + 1$ (i.e., by 2 to 4). From equations (8) and (9), under the assumption of interconnected atom ions and electron lattices, Haber derived numerical values for Cu, $n = 8.0$, and Ag, $n = 9.0$, which are actually somewhat smaller than the values in table V.

The smallness of the γ value for diamonds is very striking. It suggests that its homopolar bond is of a different type than that of the metals. Landé (ref. 71) obtained the product $m \cdot n = 27$ from the heat of sublimation (168 kcal/mole) and the compressibility ($0.16 \cdot 10^{-12}$ cm²/dyne) according to equation (7). On the other hand, for his diamond lattice model he derived a potential which begins with an attraction term of the exponent $m = 5$. The repulsion exponent n would therefore

¹¹The structures of Rb and Cs are not yet known, but it is probable that they also have space-centered crystallization.

come out small with as little probability as in table IV, namely, approximately of the same magnitude as m . It appears, therefore, that either the compressibility or the heat of sublimation of diamond substituted in the expression is too large (see section 12) or that the expression for the power force law, and therefore also the interpretation of γ according to equation (31) or (32) for homopolar bonds, such as for diamonds, is not permissible.

If for the moment diamonds are left out of consideration as doubtful, it may be said, in summarizing, that for the regularly crystallizing elements the exponents of the repulsion force derived from equation (39) have that order of magnitude which is to be expected according to the electrostatic interpretation of this force.¹²

The requirement from equation (31) that γ should be independent of the temperature is satisfied in a quite satisfactory manner. For experience has shown (ref. 73) that for the above mentioned materials, including diamond, the ratio of the expansion coefficient to the atomic heat $(\partial V/\partial T)/C_p$ at low temperature is nearly independent of T ; at higher temperatures it slowly rises. The same holds for the adiabatic compressibility $\frac{1}{V}(\frac{\partial V}{\partial p})_S$. Hence also γ can vary only slightly with T . (See further discussion in section 24.)

Polyatomic regular crystals without group formation. - Similarly simple, as in the materials discussed up to now, is the behavior of two-atom regular ionic lattices without group formation to which we may add fluorite, and perhaps with a certain restriction on account of its parameter (ref. 2, p. 304), also pyrite. For if the conditions (35) are satisfied, the equation of state (26) goes over into (25), the crystal for a pure change in volume behaves like an isotropic solid body, and from this again follows the relation (39) where V denotes the molar volume, C_v the molar heat. Since for this ionic lattice the approximate validity of the power force law with $m = 1$, $n \gg m$ has been shown with most certainty, then also equation (31)

$$\gamma = \frac{n + 2}{6}$$

may be assumed as approximately valid, and therefore we again obtain from equation (39) values for the repulsion exponent n , which we can compare with the theoretical value of Born ($n = 9$) or with the earlier value derived from the compressibility (section 11). As is shown by

¹²On an estimate of the values γ and $m \cdot n$ for argon see ref. 72.

table VI¹³, the γ for the simplest ionic lattices have the same order of magnitude as the mean value of γ for the single-atom elements, while the values of n here obtained are in relatively satisfactory agreement with $n = 9$, that is, with the values obtained by Born from the compressibility. See also the collection of values of n in table XI.

From the discussion here given it would follow that, for the ionic lattices discussed also, the values of γ , and therefore also approximately the ratio of expansion coefficient and molar heat, must be independent of temperature. That this conclusion is sufficiently well confirmed will be shown in section 24.

Born's more strict computation (ref. 3, second ed., pp. 697 and 741) gives an increase of γ with temperature. At absolute zero, for the alkali halogen salts of the NaCl type, γ is equal to about 1.5; at higher temperatures, 2.2.

Nonregular crystals. - For nonregular materials the forming of the expression (39) has a doubtful value. It does frequently give (see table VII) an indication of whether we are dealing with materials without or with group formation. In the first case (e.g., Mg, Zn, Cd, Tl, Sn, I(?)) that expression has the normal order of magnitude (again rising with increasing atomic weight) and is also a little dependent on temperature (ref. 76) because apparently here too the condition (35) is to some extent satisfied; in the second case (As, Sb, Bi, S, Te, quartz, calcite, etc.) the expression is considerably smaller, because the expansion coefficient is not proportionately small, and only at the lowest temperature when the internal vibrations ($j = 4 \dots 3p$) with their smaller γ_j (section 18) no longer possess appreciable energy does it assume the normal magnitude.¹⁴ This theoretical conclusion is also confirmed by the fact that in the case of Sb, Bi (ref. 77), and still more markedly in the case of quartz (ref. 78), the cubic expansion coefficient drops more slowly with T and C_V , so that, for example, for quartz in the interval 20.4° to 80.6° absolute $(-V \partial V / \partial T) / (C_V \partial V / \partial p)$ is more than twice as large as the value of table VII, that is, is shifted very near to the normal value for single-atom elements. For the other

¹³The figures are taken from the Landolt-Börnstein tables (ref. 63); particular account is taken of ref. 66; see also refs. 74 and 75; the majority of the expansion coefficients are cited according to Fizeau, only for NaBr, RbBr, and RbI according to Baxter and Wallace; their expansion coefficients are throughout too small, as shown by a comparison with Fizeau and therefore put in parentheses.

¹⁴For more details see ref. 56, Rapports du Conseil Solvay, p. 276ff.

materials measurements are still unavailable at lower temperatures. Such measurements would be of particular interest for calcite and aragonite. For here there appears to be an exception to the above expressed rule in regard to group formation. Aragonite, although it contains, according to W. L. Bragg (ref. 79), the same CO_3 groups as calcite, possesses a much greater volume expansion coefficient than calcite and accordingly a normal value of $(-V \partial V / \partial T) / (C_V \partial V / \partial p)$. The fact that through deformations the frequencies of the internal vibrations are more strongly influenced than in the case of calcite must be due to the different arrangement of the CO_3 groups and consequently the denser (though still more compressible!) crystal lattice of aragonite. In any case it would be expected that for aragonite the ratio $(\partial V / \partial T) / C_V$ changes relatively little with decreasing temperature. The case is similar for rutile.

The relation expressed in equation (39) belongs with the oldest in the theory of solid bodies. Guldberg (ref. 81) had set up for "ideal solid materials" the equation

$$V \frac{\partial V}{\partial T} = \text{Const} \frac{\partial V}{\partial p}$$

and remarked that it had already been found by Vogel. Later Slotte (ref. 82) and Mie (ref. 26, eq. (37)) arrived at equations of the same or similar form. Grüneisen writes equation (39) also in the form

$$\left(\frac{\partial p}{\partial u} \right)_V = \gamma$$

where $u = U/V$ denotes the energy in a cubic centimeter, that is, the energy density of the solid body. The relation can then be expressed as follows: The change of pressure with energy density at constant volume for isotropic and regularly crystallizing materials without group formation is of the same order of magnitude and almost independent of temperature.

21. Ratio of the specific heats for materials with only a single γ .
From the known thermodynamic equation for the ratio of the specific heats at constant pressure and constant volume

$$\frac{C_p}{C_V} = 1 - T \frac{\left(\frac{\partial V}{\partial T} \right)^2}{C_V \left(\frac{\partial V}{\partial p} \right)_T} = 1 - \frac{V \frac{\partial V}{\partial T}}{C_V \frac{\partial V}{\partial p}} \frac{T}{V} \frac{\partial V}{\partial T}$$

there follows, for those solid bodies for which relation (39) holds, the simple formula

$$\frac{C_p}{C_v} = 1 + \gamma \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p = 1 - \frac{T}{\theta} \left(\frac{\partial \theta}{\partial T} \right)_p \quad (40)$$

which can also be well applied in practice because the coefficient γ (of order of magnitude 2) can be considered as independent of the temperature. For the reduction of observations on C_p to C_v Nernst and Lindemann (ref. 83), again introducing the relation that $(\partial V/\partial T)/C_p$ is appreciably independent of T , employed instead of equation (40) the formula

$$C_p - C_v = aTC_p^2$$

where a must be determined for one temperature. Table VIII shows how relatively small for most single-atom elements the difference is between C_p and C_v .

22. Adiabatic change of state. - Change of the adiabatic compressibility with temperature and pressure. According to thermodynamics, during an adiabatic change in pressure there occurs a change in temperature given by

$$\frac{1}{T} \left(\frac{\partial T}{\partial p} \right)_S = \frac{1}{C_p} \left(\frac{\partial V}{\partial T} \right)_p$$

Accordingly, for all solid bodies for which equation (39) holds we have:

$$\frac{1}{T} \left(\frac{\partial T}{\partial p} \right)_S = \frac{1}{C_p} \left(\frac{\partial V}{\partial T} \right)_p = -\gamma \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S = \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_S \quad (41)$$

The relative temperature change is equal to the relative frequency change and γ times, that is, about twice as large as the compressibility. This theorem follows also directly from the fact that for these substances the entropy S is a function of θ/T , so that, at constant entropy, θ/T must likewise remain constant. It follows further that every function of θ/T remains constant also, for example C_v , whereas according to equations (13) and (41)

$$\left(\frac{\partial E}{\partial p} \right)_S = \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_S E = -\gamma \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S E \quad (42)$$

The thermal energy for adiabatic change of pressure changes in the same ratio as the frequency (θ).

The adiabatic compressibility is obtained through differentiation of the equation of state (37) with respect to p at constant entropy with account taken of equation (42) after several transformations

$$-\left(\frac{\partial V}{\partial p}\right)_S = \frac{V}{p(1 + \gamma) + G'(V) + \frac{\gamma}{V} G(V)} \quad (43)$$

From this we obtain the result that at absolute zero and for low pressures, according to equation (38a),

$$-\left(\frac{\partial V}{\partial p}\right)_{p=0, T=0} = \frac{V_0}{G'(V_0)} \quad (43a)$$

and therefore the compressibility, as already anticipated in equation (6), is

$$\kappa_0 = -\frac{1}{V_0} \left(\frac{\partial V}{\partial p}\right)_{p=0, T=0} = \frac{V_0^{\frac{m}{3}+1}}{m(n-m)A} = \frac{9r_0^{m+3}}{m(n-m)\sigma_{ma}} \quad (6)$$

On the form of this expression after introducing the Coulomb force and its experimental verification see section 11.

For arbitrary temperatures, but for such low pressures that the first term in the denominator of equation (43) can be neglected, there is obtained after several easy computations (ref. 56, Ann. d. Phys.)

$$\kappa_S = -\frac{1}{V_0} \left(\frac{\partial V}{\partial p}\right)_S = \kappa_0 \left(\frac{V}{V_0}\right)^{\frac{m+n+6}{3} - \gamma} \quad (44)$$

or approximately

$$\kappa_S = \kappa_0 \left[1 + \left(\frac{m+n+6}{3} - \gamma \right) \frac{V - V_0}{V_0} \right] \quad (44a)$$

Now because of the repeatedly employed relation between atomic heats and expansion coefficients we have to a first approximation (see section 24, eq. (54))

$$\frac{V - V_0}{V_0} = \frac{E}{Q_0}$$

if there is set

$$Q_0 = \left(\frac{C_p}{\frac{1}{V} \frac{\partial V}{\partial T}} \right)_{T=0} = \left(\frac{V\theta}{\frac{\partial \theta}{\partial p}} \right)_{T=0} \quad (45)$$

We can therefore write equation (44a) also as

$$\kappa_S = \kappa_0 \left[1 + \left(\frac{m + n + 6}{3} - \gamma \right) \frac{E}{Q_0} \right] \quad (44b)$$

From equation (44) follows

$$\frac{1}{\kappa_S} \frac{\partial \kappa_S}{\partial T} = \left(\frac{m + n + 6}{3} - \gamma \right) \frac{1}{V} \frac{\partial V}{\partial T} \quad (46)$$

The adiabatic compressibility increases with increasing temperature by an amount which is proportional to the thermal energy. The temperature coefficient of κ_S is a low-valued multiple of the volume expansion coefficient; it is thus very small.

The pressure coefficient of the compressibility is similarly obtained through logarithmic differentiation of equation (43) with respect to p at constant entropy as

$$- \frac{1}{\kappa_S} \frac{\partial \kappa_S}{\partial p} = \frac{m + n + 9}{3} \kappa_S \quad (47)$$

The adiabatic compressibility decreases with increasing pressure, the pressure coefficient being a low-valued multiple of the compressibility itself. The more compressible the material, the more strongly does its compressibility vary with the pressure.

Since as a rule the isothermal, but not the adiabatic, compressibility is observed, and experimental verification of formulas (46) and (47) cannot be given immediately. On the other hand, the theoretical checking of the small positive temperature coefficient of $\kappa_S = - \frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_S$

is important in view of equation (39) because thereby, from the theoretically required constancy of γ , the experimentally verified only slight increase of $(\partial V / \partial T) / C_p$ with increasing T follows also theoretically.

23. Isothermal change of state. Change of isothermal compressibility with temperature and pressure. - We again first seek to obtain the change of atomic frequency (θ), the atomic heat, and the thermal energy for those substances which satisfy the equation (39). According to the differentiation rule

$$\left(\frac{\partial}{\partial p} \right)_S = \left(\frac{\partial}{\partial p} \right)_T + \frac{\partial}{\partial T} \left(\frac{\partial T}{\partial p} \right)_S$$

With account taken of equations (40), (41), and (42) there follow the relations

$$\frac{1}{\theta} \left(\frac{\partial \theta}{\partial \theta} \right)_T = \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_S \frac{C_p}{C_v} = \frac{1}{C_v} \left(\frac{\partial v}{\partial T} \right)_p \quad (48)$$

$$\left(\frac{\partial C_v}{\partial p} \right)_T = - \frac{T}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_S \left(\frac{\partial C_v}{\partial T} \right)_p \quad (48a)$$

$$\left(\frac{\partial E}{\partial p} \right)_T = - \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_S \left[T \left(\frac{\partial E}{\partial T} \right)_p - E \right] \quad (48b)$$

For isothermal pressure rise, therefore, the atomic frequency increases in the ratio C_p/C_v more strongly than for adiabatic pressure rise, while the atomic heat and thermal energy decrease, for $(\partial E/\partial T)_p$ has a value between C_p and C_v (see eq. (52)), so that the expression in the brackets is positive.

The isothermal compressibility is obtained through differentiation of the equation of state (37) with respect to p at constant T or most simply from equation (44a) on the basis of the thermodynamic relation

$$\frac{\alpha_T}{\alpha_S} = \frac{C_p}{C_v} = 1 + \gamma \frac{T}{V} \frac{\partial v}{\partial T}$$

and is found to be

$$\alpha_T = \alpha_0 \left[1 + \left(\frac{m+n+6}{3} - \gamma \right) \frac{V - V_0}{V_0} + \gamma \frac{T}{V} \frac{\partial v}{\partial T} + \dots \right] \quad (49)$$

Since $T(\partial v/\partial T)$ is at any rate greater than $V - V_0$, we have

$$\frac{1}{\alpha_0} \frac{\partial \alpha_T}{\partial T} > \frac{m+n+6}{3} \frac{1}{V_0} \frac{\partial v}{\partial T} > \frac{1}{\alpha_0} \frac{\partial \alpha_S}{\partial T} \quad (50)$$

Substituting in equation (49) on account of the approximate constancy of $(\partial v/\partial T)/C_p$ according to equation (45)

$$\begin{aligned} \frac{1}{V} \frac{\partial v}{\partial T} &= \frac{C_p}{Q_0} \\ \frac{V - V_0}{V_0} &= \frac{E}{Q_0} \end{aligned}$$

there is obtained

$$\kappa_T = \kappa_0 \left[1 + \frac{m+n+6}{3} \frac{E}{Q_0} + \frac{\gamma}{Q_0} (TC_p - E) \right] \quad (49a)$$

It is seen from this equation that the third term in the brackets contributes an amount which in the range of the T^4 law for E approaches the second term in magnitude and also at medium and high temperatures makes up an appreciable fraction (for $T = \theta$ about 30 percent).

The pressure coefficient of the isothermal compressibility obtained by Grüneisen (ref. 56, Ann. d. Phys., eq. (37)) and Bridgman (ref. 33, p. 234) by substituting in equation (37) $E = 0$, which for very high pressures and low temperatures is admissible, was found to be practically as large as the pressure coefficient of the adiabatic compressibility, namely

$$-\frac{1}{\kappa} \frac{\partial \kappa}{\partial p} = \frac{m+n+9}{3} \kappa \quad (51)$$

The ratio of the pressure coefficient of the compressibility to the compressibility itself, like the ratio of the temperature coefficient of the compressibility to the volume expansion coefficient, should be a number of the order of magnitude $(m+n+9)/3$. Thus, for example

$$\begin{aligned} \text{for } m=3, n=9 \quad \frac{m+n+9}{3} &= 7 \\ \text{for } m=1, n=9 \quad &= 6,3 \end{aligned}$$

That these figures can only agree in the order of magnitude is understandable from the simplification which lies in the assumption of the power law and because of the assumption $E = 0$ in equation (51).

We will now compare the last obtained formulas with experimental results. It is to be remembered, however, that the measurement of the compressibility of solid bodies is a difficult task, while their change with temperature and pressure can be determined only with moderate accuracy.

The fact that equation (49) or (49a) is capable of giving with sufficient accuracy the variation of the compressibility with temperature at small pressures if κ_0 and $(m+n+6)/3$ are fitted to the observations was shown by Grüneisen (refs. 27, 56, and 65) through tests on copper, platinum, and iron pipes which, by increasing the internal pressure, experienced an elongation proportional to the compressibility. The temperature of the pipes was varied between -190° and 165° C.

Table IX shows that the observed and computed α agree very well. In any case it is necessary to set

$$(m + n + 6)/3 = 8.9 \text{ for copper, } 816 \text{ for platinum, and } 9.5 \text{ for iron}$$

that is, equal to values which are somewhat larger than should be expected. If, for example, we assume with Mie that $m = 3$ and n is according to table IV, there are obtained in place of the above figures 6.3, 7.4, and 5.5. For aluminum and silver, equation (49a) is no longer sufficient for higher temperature. In the same way, formula (50) can be tested for the interval -190° to 18° C. In this case Grüneisen's measurements give

$$\frac{1}{\alpha_0} \frac{\partial}{\partial T} \bigg/ \frac{1}{V} \frac{\partial V}{\partial T} = \begin{matrix} \text{Al} & \text{Ag} \\ 9.1 & 7.3 \end{matrix}$$

and these are again the right order of magnitude.

Bridgman (ref. 33), in a large experimental investigation, determined the compressibility of the metals and their change with temperature and pressure. The temperature was varied only between 30° and 75° C, and the pressure up to 12,000 kilograms per square centimeter; hence, the temperature coefficient of α is not very accurate. Table X contains for the regularly crystallizing metals the relations obtained by Bridgman

$$\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} \bigg/ \frac{1}{V} \frac{\partial V}{\partial T} \quad \text{and} \quad - \frac{1}{\alpha} \frac{\partial \alpha}{\partial p} \bigg/ \left(- \frac{1}{V} \frac{\partial V}{\partial p} \right)$$

The figures of the table fluctuate rather strongly about the theoretically obtained values. Bridgman himself ascribes the reason for this to the assumption that the exponential force laws no longer hold because they do not take into account the Schottky effect (section 11) or the compressibility of the atoms. We are inclined to believe, however, that the uncertainty of the difficult measurements including the lack of test bodies plays a large part. In particular, the pressure coefficients of gold, tungsten, and platinum appear improbably high, those of lithium, calcium, strontium, and tantalum surprisingly small.

Of particular interest are the tests of J. C. Slater (ref. 74) on the two-atom regular alkali halogen crystals for which according to section 20 the formulas (49) to (51) should likewise be valid. Since for these salts $m = 1$ and also $n \sim 9$ are better justified than for metals, a sharper testing of the formulas is possible. In table XI the compressibilities, temperature coefficients (30° to 75° C), and pressure coefficients (up to 12,000 kg/cm²) and also the expansion coefficients according to Fizeau and Baxter and Wallace have been used in order to

form the ratios of these magnitudes. Compared to the theoretical value 6.3 they appear on the average somewhat too small, but this is partially explained by the fact that κ was not extrapolated to absolute zero. If this were done, theory and experiment would be brought into quite satisfactory agreement as far as concerns the order of magnitude. Slater himself has made the extrapolation to κ_0 in order to compute from the equation

$$-\frac{1}{\kappa_0} \frac{\partial \kappa_0}{\partial p} = \frac{n+10}{3} \kappa_0 \quad (51a)$$

for the salts of the table the exponent n of the repulsion potential. We give his figures for n with all reservation in the fifth column of table XI. The fact that the order of magnitude $n = 9$ must more or less come out good is clear from what has already been said. What is particularly striking, however, is the high value of n for the lithium salts, since for the lithium ion neither $n = 9$ nor a higher exponent is theoretically well founded. The fact that the theory is here still incomplete is seen from the sixth column in which the n values computed from the compressibility itself according to equation (9) are given, not those computed by Born for room temperature (see section 11) but those by Slater from his extrapolated κ_0 . The difference between the fifth and sixth columns is particularly large for the lithium salts. The last column gives, finally, the values of n computed by the third independent method from equations (39) and (31) (see table VI).

It might be supposed from the above considerations that the relation between the temperature coefficient of the compressibility and the volume expansion coefficient of regular crystals is found similar also for the other elasticity constants. This is clearly not the case. According to tests by Voigt (ref. 84) and Steinbach (ref. 85) the temperature coefficient of the modulus of elasticity for rock salt is strongly dependent on the orientation in the crystal, although the thermal expansion is equal in all directions.

24. Change of state at constant pressure. Thermal expansion of regular crystals without group formation. - According to the energy principle the total heat imported to the gram atom at constant pressure is equal to the total change of the internal energy plus the external work, that is, according to equation (10)

$$\int_0^T C_p dT = \Phi - \Phi_0 + E + \int_0^T p dV$$

From this can be derived the equation (ref. 27, pp. 279 and 280)

$$\left(\frac{\partial E}{\partial T} \right)_p = C_v + \gamma \frac{1}{V} \frac{\partial V}{\partial T} [TC_v - E] = C_v - \frac{1}{\theta} \frac{\partial \theta}{\partial T} [TC_v - E] \quad (52)$$

The change of thermal energy with temperature at constant pressure thus lies, as can be seen by comparison with equation (40), between C_p and C_v . With increasing temperature $TC_v - E$ approaches a constant value $9/8 R\theta$, if equation (13) is used for E .

The change of atomic frequency with temperature for substances with a single γ is given by

$$\frac{1}{\theta} \left(\frac{\partial \theta}{\partial T} \right)_p = - \gamma \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (52a)$$

The thermal expansion of regular crystals without group formation which obey the equation of state (24a) is, in its essential features, determined by equation (39)

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = \gamma \frac{C_v}{V}$$

Assuming the power force law and choosing ionic lattices for which according to Born $m = 1$, $n = 9$, the absolute value of the expansion coefficient can also be approximately computed (ref. 3, second ed., p. 741). For example, for rock salt (NaCl) at ordinary temperature, setting the molar heat $C_v = 6R$ and the compressibility equal to κ_0 and neglecting its change with temperature (eq. (9)), we have

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = \frac{n+2}{6} \frac{6R}{Nr^3} \frac{9r^4}{(n+1)\alpha_m e^2} = 9 \frac{n+2}{n-1} \frac{kr}{\alpha_m e^2}$$

Hence, with $k = 1.37 \times 10^{-16}$, $e = 4.77 \times 10^{-10}$, $\alpha_m = 2.202$ (section 9), and $r = 3.55 \times 10^{-8}$

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = 120 \times 10^{-6} \quad (\text{observed} = 121 \times 10^{-6})$$

For galena (PbS) type CsCl, $\alpha_m = 4 \times 2.0354 = 8.142$, and $r = 3.74 \times 10^{-8}$, so that with $m = 1$, $n = 9$

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = 34 \times 10^{-6} \quad (\text{observed} = 60 \times 10^{-6})$$

For calcite (CaF_2) with $\alpha_m = 7.33$, $r = 3.44 \times 10^{-8}$, $C_v = 9R$, $m = 1$, and $n = 9$ there follows

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = 52 \times 10^{-6} \quad (\text{observed} = 56 \times 10^{-6})$$

Also, the law according to which the coefficient of expansion varies with temperature is contained in equation (39), as has repeatedly been mentioned. On account of the small temperature variability of α , the coefficient of expansion, for not too high a temperature, increases in proportion to the atomic heat. In particular, it increases from the value 0 at $T = 0$ in proportion to T^3 .

We shall also derive the expansion law of the above mentioned simple substances in a somewhat different form by eliminating the compressibility. Let the external pressure be vanishingly small ($p = 0$). We then expand the left side of the equation of state (37)

$$G(V) = \gamma E$$

into a series in successive powers of $\Delta = V - V_0$.

$$G(V) = G(V_0) + \Delta G'(V_0) + \frac{\Delta^2}{2!} G''(V_0) + \dots$$

taking into account the fact that according to equations (38a) and (43a)

$$G(V_0) = 0$$

$$G'(V_0) = \frac{1}{\alpha_0}$$

and further, as can easily be shown,

$$G''(V_0) = - \frac{m + n + 3}{3} \frac{1}{\alpha_0 V_0}$$

There is then obtained

$$G(V) = \frac{\Delta}{\alpha_0} \left[1 - \frac{m + n + 3}{6} \frac{\Delta}{V_0} + \dots \right] = \gamma E$$

or, if $\Delta = \gamma E \alpha_0$ is substituted in the correction term of the brackets,

$$\Delta = \frac{\gamma \alpha_0 E}{1 - \frac{m + n + 3}{6} \frac{\gamma \alpha_0}{V_0} E + \dots}$$

If according to equations (45) and (39) we introduce

$$\frac{V_0}{\alpha_0} = \left(\frac{C_p}{\frac{1}{V} \frac{\partial V}{\partial T}} \right)_{T=0} = q_0 \quad (53)$$

we have (refs. 27, p. 286, 86, and 87)

$$\frac{\Delta}{V_0} = \frac{E}{Q_0 \left[1 - \frac{m+n+3}{6} \frac{E}{Q_0} \right]} \quad (54)$$

Since Q_0 is always large compared to E , there is obtained the theorem: The relative change of volume between the temperatures θ and T increases approximately in proportion to the thermal energy. The smaller T is compared with θ , the smaller therefore E , the more strictly must the proportionality be satisfied. At higher temperature Δ increases more rapidly than E , since $(m+n+3)/6$ is a positive number.

The thermal expansion thus depends on the three constants Q_0 , θ , and $(m+n+3)/6$ (but see following section). Through suitable choice of these constants the expansion of a regular crystal without group formation must be capable of being represented. The θ obtained in this way must be identical with those which are suitable for the representation of C_V . The constant $(m+n+3)/6$ should theoretically have the value 2 to 3. That this last condition is satisfied will hardly be expected if E is computed according to the Debye formula (13) with a θ that is independent of the volume (temperature). The error thereby committed is of the same order of magnitude as the correction term in the denominator. For if E is developed into a series in $\theta - \theta_0$ and the value of E for θ_0 denoted as E_0 , there is obtained

$$\begin{aligned} E &= E_0 + (\theta - \theta_0) \left(\frac{\partial E}{\partial \theta} \right)_{\theta_0} + \dots \\ &= E_0 + \gamma \frac{E_0}{Q_0} (TC_V - E)_{\theta_0} \end{aligned}$$

Hence, equation (54) can also be written

$$\frac{\Delta}{V_0} = \frac{E_0}{Q_0 \left[1 - \frac{m+n+3}{6} \frac{E_0}{Q_0} - \gamma \frac{TC_V - E_0}{Q_0} \right]} \quad (54a)$$

If E is computed with a constant θ_0 , then according to equation (54a) there is to be expected, particularly at medium temperatures, a stronger increase of Δ than according to equation (54). This is an example of the fact that with the computation of the correction term in the denominator of the expansion formula the limit has been reached which the theory with the approximation here made can give. It will be necessary

to remain satisfied with the fact that it correctly gives the order of magnitude of the correction term.

Grüneisen has tested formula (54) and the one derived from it

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = \frac{\left(\frac{\partial E}{\partial T}\right)_p}{Q_0 \left[1 - \frac{m+n+3}{6} \frac{E}{Q_0}\right]^2} \quad (55)$$

on a number of substances having monatomic and polyatomic cubic crystal form by setting the linear expansion equal to a third of the cubic expansion and for $(\partial E/\partial T)_p$ simply taking C_V instead of the expression (52) whereby the theoretical curve for the expansion curve at medium temperatures is somewhat flattened. At larger temperature intervals there is formed the mean linear expansion coefficient

$$\frac{1}{V_0} \frac{\partial V}{\partial T} = \frac{1}{3} \frac{\Delta_2 - \Delta_1}{(T_2 - T_1)V_0}$$

where the Δ are computed from equation (54). In tables XII, XIII, and XV are collected the computed and observed results. The observations for diamond are by A. Dembowska (ref. 88); for platinum and iridium by Valentiner and Wallot (ref. 89), Scheel (ref. 90), Holborn and Day (ref. 99), Holborn and Valentiner (ref. 92), and Grüneisen (ref. 65); for copper by Dorsey (ref. 93), Lindemann (ref. 94), Henning (ref. 95), and Dittenberger (ref. 96); for gold by Dorsey, Fizeau, Müller (ref. 97), and Grüneisen; and for fluorite and pyrite by Valentiner and Wallot, and Fizeau.

The most interesting check of the theory is provided by diamond, whose $\theta = 1860$ determined by Nernst and Lindemann (ref. 98) from the specific heat is so large that the temperature intervals used in the measurement of the expansion lead to a range of the Debye C_V function which lies below the point of inflection in the well known curve representation of the function and coincides for a good part with the range of the T^3 law, which should hold between 0° and 155° absolute to less than 1 percent. The magnitude θ has the further consequence that the correction term in equation (54) does not yet come into question. The agreement between the computed and observed values in table XII therefore means the proportionality between volume expansion and thermal energy.

In the following materials the numerical factor of the correction term $(m+n+3)/6$ could be determined from the observations at higher temperature. It is obtained for copper and gold in satisfactory agreement with the values theoretically to be expected (for $m=3$ and with the n of table IV copper would give 2.7, gold 3.7); for the other materials somewhat larger values, as, from what was said above, are not surprising.

It is worth remarking that the good representation of the expansion through formula (54) for the polyatomic crystals fluorite and pyrite whose molecular heats according to Eucken and Schwes (ref. 99) can be represented by a Debye function with the θ of table XV. In the case of pyrite this success was not necessarily expected since a possibility of group formation was not excluded.

In accordance with the examples given it appears that not only the monatomic but also the polyatomic regular crystals without group formation follow the law of thermal expansion expressed in equation (54), where, however, the numerical factor of the correction term must be empirically determined and agrees only approximately with the theoretical $(m + n + 3)/6$. A definitive conclusion will be possible only when further results of measurements are available.

25. Computation of the limiting frequency (θ) from the ratio of the expansion coefficient to the atomic heat. - Of the three constants which were found to be necessary for the representation of the thermal expansion in the preceding section, θ and Q_0 are not independent of each other for single-atom regular crystals. From the equations (29a) and (53) there follows namely for the limiting frequency

$$v^2 = \gamma z^2 N^{2/3} \frac{Q_0}{M V_0^{2/3}} = \gamma z^2 \frac{Q_0}{M r_0^2} \quad (56)$$

where $\gamma z^2 \sim 0.26$, and therefore for $T = 0$

$$\theta_0 = C \sqrt{\frac{Q_0}{M V_0^{2/3}}} \quad (56a)$$

where

$$C = \frac{h}{k} N^{1/3} \sqrt{\gamma z_0^2}$$

so that with account taken of equations (30) and (32)

$$C = \frac{h}{k} N^{1/3} \left[\frac{3}{8\pi^2} \frac{(n+1)(n+2)\psi_n - (m+1)(m+2)\psi_m}{n-m} \right]^{1/2}$$

C is therefore determined by the laws of force. Empirically the best value obtained was $C = 14.37$, if Q_0 is reckoned in gram-calories. For the materials in tables XII and XIII the values of θ_0 computed from Q_0 according to equation (56a) are in table XIV compared with the "observed" values, that is, with those given in tables XII and XIII determined from the variation of the expansion coefficient with temperature.

26. Thermal expansion of nonregular crystals.¹⁵ - In every homogeneous crystal there are three mutually perpendicular directions which during the thermal expansion may change their position in space but after the deformation are again mutually perpendicular. These are the principal axes of the deformation ellipsoid which has arisen from a sphere with radius l through the temperature change. They are called "thermal axes" or "principal axes of the thermal dilation". In their initial position they may be assumed to coincide with the axes of a rectangular xyz coordinate system. To each axis corresponds a particular "principal expansion coefficient" (α_x , α_y , and α_z) if there is set briefly

$$\alpha = \frac{1}{l_0} \frac{\partial l}{\partial T}.$$

Whereas for the crystals of the regular system, like for isotropic bodies, $\alpha_x = \alpha_y = \alpha_z$, for the nonregular crystals the α values depend on the direction. The dependence corresponds to the symmetry of the crystal.

In the crystals of the hexagonal, trigonal, and tetragonal system the position of the thermal axes is always the same. One of the thermal axes (z) coincides with the crystallographic c -axis. The other two (x and y) may be any two axes perpendicular to the c -axis and to each other, since in the plane perpendicular to the c -axis the linear thermal expansion is independent of the direction ($\alpha_x = \alpha_y$; $\alpha_z \gtrless \alpha_x$). The deformation ellipsoid is an ellipsoid of rotation.

In the crystals of the rhombic, monoclinic, and triclinic systems the principal expansion coefficients are different from one another. The deformation ellipsoid is a triaxial ellipsoid.

In the crystals of the rhombic system the position of the thermal axes is independent of the temperature, since for each temperature they coincide with the crystallographic axes. In the crystals of the monoclinic system only one of the thermal axes has a position independent of the temperature; it coincides with the b -axis. The other two axes lie in the plane perpendicular to the b -axis. Its position must be specially determined for each temperature. In the crystals of the triclinic system the position of all three thermal axes is different for each temperature; it must be obtained separately for each temperature change.

¹⁵All that was known up to the year 1920 on the thermal expansion of minerals, rocks, and artificially produced materials of corresponding composition is found carefully collected in ref. 100. From this work is also taken the initial discussion of this section essentially unaltered. For further results of measurement see ref. 101.

The volumetric expansion coefficient $\frac{1}{V_0} \frac{\partial V}{\partial T}$ is approximately for the regular system, 3α ; for the hexagonal, trigonal, and tetragonal systems, $\alpha_x + \alpha_y + \alpha_z$. Also, the sum of the linear expansion coefficients in three arbitrary mutually perpendicular directions gives $\frac{1}{V_0} \frac{\partial V}{\partial T}$ (ref. 102).

The linear expansion coefficient in any direction which forms with the principal dilatation axes x, y, z the angles ϕ_x, ϕ_y, ϕ_z is given by the formula (ref. 102):

$$\alpha = \alpha_x \cos^2 \phi_x + \alpha_y \cos^2 \phi_y + \alpha_z \cos^2 \phi_z \quad (57)$$

The thermal expansion is thus completely determined if the three constants α_x, α_y , and α_z are known, or in the case of the hexagonal, trigonal, and tetragonal systems the two $\alpha_x = \alpha_y$ and α_z , from which there is then computed

$$\alpha = \alpha_x \sin^2 \phi_z + \alpha_z \cos^2 \phi_z \quad (57a)$$

For the principal expansion coefficients the thermodynamic formulas hold

$$V\alpha_x = - \left(\frac{\partial S}{\partial X_x} \right)_T$$

$$V\alpha_y = - \left(\frac{\partial S}{\partial Y_y} \right)_T$$

$$V\alpha_z = - \left(\frac{\partial S}{\partial Z_z} \right)_T$$

where the entropy S of the mole is given by equation (23). S depends on X_x, \dots only in so far as θ_j depends on them. There is obtained

$$V\alpha_x = R \sum_{j=1}^3 \int \frac{\partial \log \theta_j}{\partial X_x} C\left(\frac{\theta_j}{T}\right) \frac{d\theta_j}{4\pi} + R \sum_{j=4}^{3p} \frac{\partial \log \theta_j}{\partial X_x} H\left(\frac{\theta_j}{T}\right) \quad (58)$$

Since the functions C and H defined through equations (12a) and (13a) vanish for $T = 0$, the same holds true for α_x, α_y , and α_z , as must be the case since the expansion coefficients of every chemically homogeneous solid body must for decreasing temperature approach without restriction the value zero (ref. 103). In general, however, there can be no question

of an even approximate proportionality of the principal expansion coefficient to the molar heat (eq. (17a)). (See conclusion of section 17 and section 18 and the remarks on nonregular substances in section 20).

27. Thermal expansion of hexagonal crystals (zinc, cadmium). - The further treatment and application of equation (58) is possible only under simplifying assumptions, such as for example were introduced by Grüneisen and Goens (ref. 104) for the purpose of representing the thermal expansion of zinc and cadmium crystals. These crystals belong to the hexagonal system and form no atom groups. The second term, referring to the internal vibrations, on the right side of equation (58) therefore drops out, x and y are equal, and z is along the axis direction.

The change of pressure ∂X_x or ∂Z_z leads to the deformations x_x , y_y , and z_z . Hence

$$\frac{\partial \log \theta_j}{\partial X_x} = \frac{\partial \log \theta_j}{\partial x_x} \frac{\partial x_x}{\partial X_x} + \frac{\partial \log \theta_j}{\partial y_y} \frac{\partial y_y}{\partial X_x} + \frac{\partial \log \theta_j}{\partial z_z} \frac{\partial z_z}{\partial X_x}$$

and similarly for Z_z . Now for a hexagonal system (ref. 102)

$$\frac{\partial x_x}{\partial X_x} = -s_{11}$$

$$\frac{\partial y_y}{\partial X_x} = -s_{12}$$

$$\frac{\partial z_z}{\partial X_x} = -s_{13}$$

where the s_{pq} are the "principal elasticity moduli" in the notation of Voigt. Substituting finally according to equation (34) the $(r_j)_{xx}$ there is obtained

$$\frac{\partial \log \theta_j}{\partial X_x} = (r_j)_{xx} (s_{11} + s_{12}) + (r_j)_{zz} s_{13}$$

$$\frac{\partial \log \theta_j}{\partial Z_z} = 2(r_j)_{zz} s_{13} + (r_j)_{zz} s_{33}$$

Substituting these expressions into equation (58) there is obtained

$$\begin{aligned} \alpha_x &= (s_{11} + s_{12}) q_{xx} + s_{13} q_{zz} \\ \alpha_z &= 2s_{13} q_{xx} + s_{33} q_{zz} \end{aligned} \tag{59}$$

where

$$\left. \begin{aligned} q_{xx} &= \frac{R}{V} \sum_{j=1}^3 \int (r_j)_{xx} c\left(\frac{\theta_j}{T}\right) \frac{d\Omega}{4\pi} \\ q_{zz} &= \frac{R}{V} \sum_{j=1}^3 \int (r_j)_{zz} c\left(\frac{\theta_j}{T}\right) \frac{d\Omega}{4\pi} \end{aligned} \right\} \quad (60)$$

are the so-called thermal pressure coefficients in the directions perpendicular and parallel to the hexagonal axes.

The absolute values of the principal expansion coefficients are therefore determined very largely by the magnitude of the principal elasticity moduli s_{pq} ; their variation with the temperature, however, is by the variation of the thermal pressure coefficients since s_{pq} changes only relatively little with the temperature. Through the interplay of these effects remarkable phenomena may at times arise, as is shown by the examples of zinc and cadmium. These metals have as single crystals a very strong elastic anisotropy (refs. 50, 105, and 106); hence values of θ are strongly dependent on the direction. In the z-direction the θ_j are small; at right angles to this direction they are large. As regards the r values, little that is definite can be said theoretically. They depend similarly on the direction, in the case under consideration probably in such manner that r_{zz} has a maximum in the z-direction, and r_{xx} a maximum perpendicular to z. The values of the function C therefore enter q_{xx} and q_{zz} with different weights in the space averaging. Without going into a more detailed discussion of the space integrals, we may try to give an approximate account of the relations discussed by setting

$$\left. \begin{aligned} q_{xx} &= \frac{3R}{V} \bar{r}_x c\left(\frac{\bar{\theta}_x}{T}\right) \\ q_{zz} &= \frac{3R}{V} \bar{r}_z c\left(\frac{\bar{\theta}_z}{T}\right) \end{aligned} \right\} \quad (60a)$$

where the \bar{r}_x , \bar{r}_z , $\bar{\theta}_x$, and $\bar{\theta}_z$ represent as yet unknown mean values. In this way a large simplification of formulas (59) is attained. The thermal pressure coefficients q are now proportional to simple Debye atomic heat functions. The thermal expansion parallel and perpendicular to the hexagonal axes can be represented by the above named four constants as long as at least the elastic constants s_{pq} may be assumed independent of T , that is, at not too high a temperature.

Table XVI gives the observed principal expansion coefficients of zinc and cadmium and the values computed from equations (59) and (60a) according to Grüneisen and Goens and also the volume expansion coefficients $\alpha_z + 2\alpha_x$. Table XVII contains the values of s_{pq} used for the computations and similarly measured by the above mentioned authors and the constants $\bar{\gamma}$ and $\bar{\theta}$ fitted to the observations. In figures 3 and 4 the dotted curves correspond to the observations, the solid curves to the computation. The directions parallel and perpendicular have different scales so that the large difference between α_x and α_z does not appear striking, but the entirely different behavior with dropping temperature is evident: for α_x a rapid drop up to negative values (also observed for zinc), for α_z a rise up to a maximum (observed for both metals) and then an extremely rapid drop to zero.

The $\bar{\gamma}_x$ and $\bar{\gamma}_z$ have the order of magnitude to be expected for crystals without group formation (see table VII, last column, values for zinc and cadmium); the $\bar{\theta}_x$ and $\bar{\theta}_z$ are somewhat larger than would be expected according to the variation of the atomic heat. Up to the present there is no possibility of determining these mean values theoretically.

The above presentation in formulas of the theoretical expansion of zinc and cadmium may be clarified in words as follows: If, starting from absolute zero where all atomic degrees of freedom of vibrations are without any heat energy, we imagine a zinc or cadmium crystal to be heated somewhat, then an appreciable energy will at first be transferred to the slower vibrations parallel to the axes and only with further increase will gradually be distributed to other directions up to the rapid vibrations perpendicular to the axes. The thermal expansion in any direction is the consequence of the vibrations in this direction, because according to Debye owing to the deviation from Hooke's law through the vibration a shift of the vibration center must occur (section 6); therefore at the initial heating from absolute zero the vibrations will first give an expansion parallel to the axes which is relatively large because in this direction the elastic work of expansion (s_{33}) is large. With this thermal expansion, however, is connected an elastic transverse contraction perpendicular to the axis (according to the magnitude of the constant s_{13}), which appears as a negative expansion coefficient, because in this direction there are as yet no appreciable heat vibrations. With further temperature rise another process is superimposed on the one so far described: the positive thermal expansion perpendicular to the axis, which corresponding to the small elastic expansion coefficient perpendicular to the axis (s_{11}) is only small, but still compensates more and more the negative elastic expansion and finally reverses the sign; and the elastic transverse contraction parallel to the axis (s_{13}), which retards the rate of rise of α_{11} and produces a maximum of its value.

The trend of the curves for $\alpha_{||}$ and α_{\perp} at low temperature thus gives a clear proof for the requirement of the quantum theory that vibrations of higher frequency should begin to take up energy only at higher temperatures than vibrations of low frequency.

As is known, zinc and cadmium in the polycrystalline state produce a ringing noise at rapid cooling (e.g., to -190°C) and for every rapid temperature alternation often long lasting effects of the thermal expansion. These phenomena are not encountered in the case of single crystals, and thus are probably connected with the internal stresses and slips arising between the crystallites oriented without any order because of their strong anisotropy.

28. The ratio of the mean vibration amplitude to the interatomic distance (refs. 56 and 107). - The question of the true magnitude or space filling of the atom (section 5) is evidently closely connected with the question of the magnitude of the vibration amplitudes. If the mean amplitude \bar{e} of the individual atom at sufficiently high temperature T is defined by the equation¹⁶

$$E = \frac{8}{3} \pi^2 \nu^2 \bar{e}^2 M \quad (61)$$

where ν is the Debye limiting frequency and there is set according to equation (56)

$$M\nu^2 = \gamma z^2 \frac{Q_0}{r_0}$$

and according to equation (54)

$$E = Q_0 \frac{\Delta}{V_0} \left[1 - \frac{m+n+3}{6} \frac{\Delta}{V_0} \right]$$

there is obtained

$$\frac{\bar{e}}{r_0} = \sqrt{\frac{\Delta}{V_0} \frac{1 - \frac{m+n+3}{6} \frac{\Delta}{V_0}}{\frac{8}{3} \pi^2 \gamma z^2}}$$

¹⁶If the energy of a sine vibration of amplitude e is namely set equal to the mean energy of a Planck oscillator and the mean value \bar{e} is formed by integrating over the elastic frequency spectrum, there is obtained for high temperatures $\bar{e}^2 = \frac{9}{8} \frac{kT}{\pi^2 \nu^2 \mu}$, from which, with $E = 3NkT$ and $M = N\mu$ there follows equation (61).

or neglecting the correction term in the numerator and substituting the larger z_0^2 instead of z^2 in the denominator

$$\frac{\bar{e}}{r_0} = \sqrt{\frac{\Delta}{\frac{8}{3} \pi^2 \gamma z_0^2 v_0}} \quad (62)$$

The numerical factor $\frac{8}{3} \pi^2 \gamma z_0^2$ has approximately the value 8 for single-atom regular substances. As long as this can be considered as constant for various substances the following theorems accordingly hold true:

1. The ratio of the mean amplitude to the mean distance of neighboring atoms increases with the temperature approximately as the square root of the volume increases.

2. For different single-atom regular crystals, for equal relative expansion, the vibration amplitude is approximately the same fraction of the atomic distance.

Now the melting point T_s according to reference 56 is a temperature for which in order of magnitude

$$\left(\frac{\Delta}{v_0}\right)_{T=T_s} = 0.08 \quad (63)$$

Hence

$$\left(\frac{\bar{e}}{r_0}\right)_{T=T_s} = 0.105 \quad (64)$$

The mean amplitude even at the melting point thus amounts to only about 10 percent of the shortest atomic distance, which is somewhat larger than r_0 .

If, with F. A. Lindemann (ref. 108), it is assumed that during melting the "true" ranges (section 5) of neighboring atoms meet, then from the above derived number we must conclude as to a rather large, for different elements approximately equal, ratio of the space filling of the atoms to their so-called atomic volume. It is to be remembered, however, that \bar{e} represents a mean value of the amplitude which may be considerably exceeded in the vibrations of individual atoms. In this way a compromise must be sought with the result of section 5 according to which the space filling is relatively small.

The change of the amplitude with temperature and pressure can also be computed from equation (61). There is obtained

$$\frac{1}{\bar{e}} \left(\frac{\partial \bar{e}}{\partial T} \right)_p = \frac{1}{2} \frac{1}{E} \left(\frac{\partial E}{\partial T} \right)_p - \frac{1}{\theta} \left(\frac{\partial \theta}{\partial T} \right)_p$$

so that according to equations (52), (52a), and (40)

$$\left(\frac{\partial \log \bar{e}}{\partial \log T} \right)_p = \frac{1}{2} \frac{TC_p}{E} - \frac{1}{2} \frac{\partial \log \theta}{\partial \log T} = \frac{1}{2} \frac{TC_p}{E} + \frac{1}{2} \left(\frac{C_p}{C_v} - 1 \right)$$

In an adiabatic change in pressure E/v remains constant; hence, from (61)

$$\frac{1}{\bar{e}} \left(\frac{\partial \bar{e}}{\partial p} \right)_s = - \frac{1}{2} \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_s = - \frac{1}{2} \frac{1}{C_p} \left(\frac{\partial v}{\partial T} \right)_p = \frac{\gamma}{2} \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_s$$

Since the volume compressibility is three times the linear compressibility and $\gamma \sim 2$, there is obtained the result that in an adiabatic pressure rise the amplitude decreases relatively three times as strongly as the interatomic distance. In absolute value, however, the change in amplitude is still considerably smaller than the change in distance, so that in adiabatic compression there is an approach of the vibration spaces of the atoms.

In isothermal compression the relative change in amplitude is greater than in adiabatic in the ratio $1 + (\partial \log \bar{e} / \partial \log T)_p$.

29. Relations of the melting temperature to other properties of the solid material. Lindemann's melting point formula. - The relation very long known between the melting temperature and the expansion coefficient finds rational expression through equation (63) and becomes physically understandable from the discussion of section 28.

Of more importance is a relation found by F. A. Lindemann (ref. 108) between the melting point and the limiting frequency of the atom. If in equation (61) there is substituted $E = 3RT_s$ and according to equation (64) $\bar{e} = 0.105 r_0$, there is obtained for the atomic frequency at the melting point

$$v_s^2 = \frac{9R}{8\pi^2 0.105^2} \frac{T_s}{Mr_0^2} = \frac{9RN^{2/3}}{8\pi^2 0.105^2} \frac{T_s}{MV_0^{2/3}} \quad (65)$$

which gives

$$\nu_s = 2.5 \cdot 10^{12} \sqrt{\frac{T_s}{MV_0^{2/3}}}$$

$$\theta_s = 119 \sqrt{\frac{T_s}{MV_0^{2/3}}}$$

Since the frequency decreases about twice as fast with the temperature as the volume increases, ν_0 and θ_0 are by about 16 percent larger. The formula has been found in good agreement with experiment.

Another relation between melting point and compressibility is obtained through elimination of the atomic frequency from formulas (29a) and (65). In this way there is obtained¹⁷

$$\alpha \sim \frac{V_0}{T_s}$$

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¹⁷Apparently in better agreement is the somewhat modified empirical formula of Richards (ref. 64) $\alpha = 0.00021 M^{-1/3} (T_s - 500)$.

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TABLE I. - PERIODIC SYSTEM OF THE ELEMENTS WITH THEIR CORRESPONDING CRYSTAL SYSTEMS

Period	Group	I	II	III	IV	V	VI	VII	VIII
		a	b	a	b	a	b	a	b
I	1 H 2 He	3 Li c bc	4 Be hex	5 B	6 C c (Diamond) β) trig (Graphite)	7 N c	8 O hex	9 F	
II	10 Ne	11 Na c bc	12 Mg hex	13 Al c fc	14 Si c	15 P c (white)	16 S α) rhomb β) monocl	17 Cl	
III	18 Ar c fc	19 K c bc	20 Ca c fc	21 Sc	22 Ti hex	23 V c bc	24 Cr c bc	25 Mn α and β) c γ) tetrag	26 Fe α, β, γ) c bc γ) c fc
IV	36 Kr	37 Rb c fc	38 Sr	39 Y	40 Zr hex	41 Nb c	42 Mo c bc	43 —	44 Ru hex
V	54 Xe	55 Cs	56 Ba	57 La	58 Ce α) hex β) c fc	59-71 Rare-earth elements	52 Te trig	53 I rhomb	46 Pd c fc
VI	86 Rn	87 —	88 Ra	89 Ac	90 Th c fc	91 Pa	92 U	74 W c bc	76 Os hex
								75 —	77 Ir c fc
								84 Po	78 Pt c fc
								85 —	

TABLE II. - DISTRIBUTION OF ELEMENTS AND COMPOUNDS OVER DIFFERENT CRYSTAL SYSTEMS

Crystal system	Element, percent	Inorganic compounds					Organic compounds, percent
		2 Atoms, percent	3 Atoms, percent	4 Atoms, percent	5 Atoms, percent	More than 5 atoms, percent	
Cubic	57	68.5	42	5	12	5.8	2.5
Hexagonal	31	19.5	11	35	38	14.6	4.0
Tetragonal	7	4.5	19	5	6	7.0	5.0
Rhombic	4	3.0	23.5	50	36	27.3	33.0
Monoclinic	1	4.5	3	5	6	37.3	47.5
Triclinic	0	0	1.5	0	2	8.0	7.0
Number of cases investigated	56	67	63	20	50	673	585

TABLE III. - TESTING OF ADDITION LAW OF "ATOM SPHERE RADII"

	Mole volume		
	<u>Molecular weight</u> Density	Computed from NaCl type	Computed from space-centered type
CsCl	41.80	(55.28)	42.56
CsBr	47.40	(63.28)	48.72
CsI	56.85	(76.25)	58.70

TABLE IV. - THERMOELASTIC PROPERTIES OF REGULARLY CRYSTALLIZING ELEMENTS (20° C)

[The figures are taken partly from refs. 33 and 63 to 68. The compressibilities hold for a pressure of zero. All values hold for room temperature.]

	Group of the periodic system	Atomic weight, M	Density, S	Atomic volume, V	Expansion coefficient, $\frac{1}{V} \times \frac{\partial V}{\partial T} \times 10^6$	Compressibility, $-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \times 10^{12}$	Atomic heat, $C_V \times 10^{-7}$	$V \frac{\partial V}{\partial T} - \frac{\partial V}{\partial P} = \gamma$	n from eq. (31.)
Li	I	6.94	0.546	12.7	180	8.9	22.0	1.17	5.0
Na		23.00	.971	23.7	216	15.8	26.0	1.25	5.5
K		39.10	.862	45.5	250	33	25.8	1.34	6.0
Rb		85.5	1.53	56.0	270	40	25.6	1.48	6.9
Cs		132.8	1.87	71.0	290	61	26.2	1.29	5.7
Cu		63.57	8.92	7.1	49.2	.75	23.7	1.96	9.8
Ag		107.88	10.49	10.3	57	1.01	24.2	2.40	12.4
Au		197.2	19.2	10.3	43.2	.59	24.9	3.03	16.2
Al		26.97	2.70	10.0	67.8	1.37	22.8	2.17	11.0
Si		28.09	2.33	12.0	29.1	.16	5.66	1.10	4.6
(diamond)	IV	12.00	3.51	3.42					
Pb	V	207.2	11.35	18.2	86.4	2.30	25.0	2.73	14.4
P (white)		31.04	1.83	17.0	370	20.5	24	1.28	5.7
Ta	VI	181.5	16.7	10.9	19.2	.49	24.4	1.75	8.5
Mo		96.0	10.2	9.5	15.0	.36	25.2	1.57	7.4
W	VII	184.0	19.2	9.6	13.0	.30	25.8	1.62	7.7
Mn		54.93	7.37	7.7	63	.84	23.8	2.42	12.5
Fe	VIII	55.84	7.85	7.1	33.6	.60	24.8	1.60	7.6
Co		58.97	8.8	6.7	37.2	.55	24.2	1.87	9.2
Ni		58.68	8.7	6.7	38.1	.54	25.2	1.86	9.3
Pd		106.7	12.0	8.9	34.5	.54	25.6	2.23	11.4
Pt		195.2	21.3	9.2	26.7	.38	25.5	2.54	13.2

^aThe compressibility of diamond later found by Adams and Williamson (ref. 69), which was still considerably higher, was 0.19×10^{-12} . We hold to the first determined value, since the compressibility of the reference material, steel, of 0.60×10^{-12} , without account taken of the high pressure interval employed (2000 to 10,000 megabars) should be too high by about 0.03×10^{-12} .

TABLE V. - REPULSION EXPONENTS

(a) Space-centered cubes			(b) Face-centered cubes		
	γ	n		γ	n
Li	1.17	5.0	Al	2.17	11.0
Na	1.25	5.5	Co	1.87	9.2
K	1.34	6.0	Ni	1.88	9.3
Rb	1.48	6.9	Cu	1.96	9.8
Cs	1.29	5.7	Pd	2.23	11.4
Fe	1.60	7.6	Ag	2.40	12.4
Mo	1.57	7.4	Pt	2.54	13.2
Ta	1.75	8.5	Au	3.03	16.2
W	1.62	7.7	Pb	2.73	14.4

TABLE VI. - THERMOELASTIC PROPERTIES OF REGULARLY CRYSTALLIZING COMPOUNDS WITHOUT GROUP FORMATION

	Molecular weight, M	Density, S	Molecular volume, V	Expansion coefficient, $\frac{1}{V} \times \frac{\partial V}{\partial T} \times 10^6$	Compressibility, $-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \times 10^{12}$	Atomic heat, $C_V \times 10^{-7}$	$V \frac{\partial V}{\partial T} = \gamma$ $-\frac{\partial V}{C_V \partial p} = \gamma$	n from eq. (31)
NaCl	58.46	2.16	27.1	121	4.2	47.6	1.63	7.8
NaBr	102.9	3.20	32.1	(120)	5.1	48.4	(1.56)	(7.4)
KCl	74.6	1.99	37.5	114	5.6	47.7	1.60	7.6
KBr	119.0	2.75	43.3	126	6.7	48.4	1.68	8.1
KI	166.0	3.12	53.2	128	8.6	48.7	1.63	7.8
PbBr	165.4	3.35	49.4	(107)	7.9	48.9	(1.37)	(6.2)
RbI	212.4	3.55	59.8	(102)	9.6	49.5	(1.41)	(6.5)
AgCl	143.3	5.55	25.8	99	2.4	50.2	2.12	10.7
AgBr	187.8	6.32	29.7	104	2.7	50.1	2.28	11.7
CaF ₂	78.1	3.18	24.6	56.4	1.24	65.8	1.70	8.2
(fluorspar)								
FeS ₂	120.0	4.98	24.1	26.2	.71	59.9	1.47	6.8
(Pyrite)								
PbS	239.3	7.55	31.7	60	1.96	50	1.94	9.6
(galena)								

TABLE VII. - THERMOELASTIC PROPERTIES OF NONREGULAR ELEMENTS AND COMPOUNDS, PARTLY WITHOUT, PARTLY WITH GROUP FORMATION. ALL FIGURES HOLD FOR ROOM TEMPERATURE^a

	Group of the periodic system; structure	M	S	V	$\frac{1}{V} \frac{\partial V}{\partial T} \times 10^6$	$\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \times 10^{12}$	$C_V \times 10^{-7}$	$V \frac{\partial V}{\partial T} \cdot \frac{\partial V}{C_V \partial P}$
Mg	II	24.32	1.69	14.4	75	3.0	23.8	1.51
Zn	hex	65.37	7.13	9.2	90	1.72	24.0	2.01
Cd	III	112.4	8.65	13.0	93	2.25	24.5	2.19
Tl	tetrag	204.0	11.8	17.3	90	2.3	24.8	2.73
Sn	IV	118.7	7.30	16.3	64	1.91	25.5	2.14
As	V	74.96	5.7	13.2	16	4.5	24.3	.19
Sb	trig	120.2	6.68	18.0	33	2.7	24.1	.92
Bi	rhomb	209.0	9.80	21.3	40	2.97	25.2	1.14
S	VI	32.07	2.07	15.5	180	12.9	21.6	1.00
Te	trig	127.5	6.2	20.6	52.8	5.18	25.2	.83
I	VII	126.9	4.9	25.9	250	13.0	24.1	2.07
SiO ₂ (quarz)	trig	60.3	2.649	22.8	36.2	2.67	43.7	.71
TiO ₂ (rutile)	tetrag	80.1	4.250	18.9	23.7	.58	59	1.3
SiO ₂ ZrO ₂ (zircon)	tetrag	182.9	4.6	39.8	9.1	.85	100	.43
Be ₃ Al ₂ (SiO ₃) ₆ (beryl)	hex	539.3	2.703	199	^b 1.2	.57	447	.09
CaCO ₃ (calcspat)	trig	100.07	2.71	37.0	15.4	1.34	80.5	.51
CaCO ₃ (aragonite)	rhomb		2.932	34.2	61.9	1.53	81.5	1.68

^aSee remarks on tables 4 and 6. On thermal expansion refer to the tables of ref. 80. Here is also found in vol. 4 the proof that the expansion coefficient of zircon taken over in the German literature from Pogg. Ann. vol. 135, p. 372, 1868 is according to Fizeau 10 times too large through the dropping of a zero. The value above is taken from the original treatise in the C.R., which evidently is the correct one.

^bMeasured with not quite agreeing values by Fizeau and Benoit.

TABLE VIII. - RATIOS OF SPECIFIC HEATS
AT CONSTANT PRESSURE AND CONSTANT
VOLUME AT 20° C AND LOW PRESSURE

Element	C_p/C_v	Element	C_p/C_v
Li	1.056	Ta	1.010
Na	1.079	Mo	1.007
K	1.10	W	1.006
Rb	1.11	Mn	1.044
Cs	1.11	Fe	1.016
Cu	1.028	Co	1.020
Ag	1.040	Ni	1.021
Au	1.038	Pd	1.022
Al	1.043	Pt	1.020
Pb	1.067		

TABLE IX. - CHANGE OF COMPRESSIBILITY WITH TEMPERATURE

$\kappa \times 10^{12} [\text{C.G.S}]$	-273°	-190°	+17°	+131°	+165° C
Cu	Observed	0.718	0.773	0.815	0.828
	Computed	0.710	.717	.815	.825
Pt	Observed	.374	.392	.401	.404
	Computed	.371	.391	.401	.404
Fe	Observed	.606	.633	.664	.675
	Computed	.600	.638	.663	.672

TABLE X. - TEMPERATURE AND PRESSURE COEFFICIENTS OF COMPRESSIBILITY ACCORDING TO BRIDGMAN

Group of the periodic system	$\alpha \times 10^6 (30^\circ)$ for $p = 0$ cm^2/kg	$\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} / \frac{1}{V} \frac{\partial V}{\partial T}$	$-\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} / \alpha$	Group of the periodic system	$\alpha \times 10^6 (30^\circ)$ for $p = 0$ cm^2/kg	$\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} / \frac{1}{V} \frac{\partial V}{\partial T}$	$-\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} / \alpha$
I				IV			
Li	8.7	3.8	2.6	Pb	2.4	6.3	4.6-6.1
Na	15.6	4.4	4.9	Ta	.48	2.6	2.2
K	35.6	5.6	9.8	Mo	.35	5.7	16-21
Cu	.72	4.2-9.4	10.0	W	.30	1.2-13.7	32-35
Ag	.99	6.7	9.0	U	.97	---	5.4
Au	.58	---	18.7	Fe	.587	6.3	12
Ca	5.7	7.9	2.9	Co	.54	8.9	14
Sr	8.2	---	2.2	Ni	.53	6.0	15
Al	1.34	7.6-13.2	4.0-5.7	Pd	.52	3.4	15
Ge	1.38	---	7.2	Pt	.36	9.2	28

TABLE XI. - COMPRESSIBILITY, TEMPERATURE, AND PRESSURE COEFFICIENTS ACCORDING TO

J. C. SLATER. EXPANSION COEFFICIENTS OF NaCl, KCl, KBr, KI ACCORDING TO

FIZEAU, NaBr and RbI ACCORDING TO BAXTER AND WALLACE^a

	$\alpha \times 10^{12} (30^\circ)$ for $p = 0$ cm^2/dyne	$\frac{1}{\alpha} \frac{\partial \alpha}{\partial T} / \frac{1}{V} \frac{\partial V}{\partial T}$	$-\frac{1}{\alpha} \frac{\partial \alpha}{\partial p} / \alpha$	α calculated from eq. (51a)	α calculated from eq. (9)	α calculated from eqs. (31) and (39)
LiF	1.53	---	7.6	14.3	5.9	---
LiCl	3.41	---	5.8	11.9	8.0	---
LiBr	4.31	---	5.7	12.8	8.7	---
NaCl	4.20	5.6	5.2	9.8	9.1	7.8
NaBr	5.08	6.2	5.0	9.5	9.5	(7.4)
KF	3.31	---	6.1	8.9	7.9	---
KCl	5.63	4.2	4.7	6.5	9.7	7.6
KBr	6.70	4.8	4.7	7.1	10.0	8.1
KI	8.54	4.7	4.6	6.8	10.5	7.8
RbBr	7.94	---	4.4	6.2	10.0	(6.2)
RbI	9.58	6.7	4.5	6.8	11.0	(5.5)

^aUncertain, see above.

TABLE XII. - EXPANSION COEFFICIENT OF DIAMOND

	ΔT	$\frac{1}{l_0} \frac{\partial l}{\partial T} \times 10^6$		Computed- Observed
		Computed	Observed	
Diamond $\theta = 1860$ $Q_0 = 457 \text{ kcal}$	84.8/194.1	0.16	0.18	-02
	194.1/273.2	.61	.58	+03
	273.2/296.2	.97	.97	\pm
	296.2/328.0	1.17	1.17	\pm
	328.0/351.1	1.37	1.45	-08

TABLE XIII. - THERMAL EXPANSION COEFFICIENT OF SEVERAL METALS

	T	$\frac{1}{l_0} \frac{\partial l}{\partial T} \times 10^6$		Computed-Observed	Δm	$\frac{1}{l_0} \frac{\partial l}{\partial T} \times 10^6$		Computed-Observed
		Computed	Observed			Computed	Observed	
Platinum $\theta = 230$; $Q_0 = 231$ kcal; $\frac{m+n+3}{6} = 4.8$	96.2	6.62	6.66	-04	289/329	8.85	8.95	-10
	139.2	7.64	7.57	+07	329/373	9.02	9.11	-09
	190.9	8.24	8.16	+08	289/523	9.18	9.23	-05
	217.2	8.42	8.28	+14	523/773	9.87	9.84	+03
	225.9	8.48	8.42	+06	773/1023	10.60	10.52	+08
	247.1	8.60	8.57	+03	1023/1273	11.38	11.1-11.4	
	267.2	8.70	8.74	-04				
	283.6	8.76	8.85	-09				
Iridium $\theta = 283$; $Q_0 = 307$ kcal; $\frac{m+n+3}{6} = 6.5$	98.0	4.44	4.43	+01	90/290	5.77	5.71	+06
	132.3	5.27	5.22	+05	290/373	6.62	6.58	+04
	209.2	6.09	5.85	+24	295/2003	8.66	8.75	-09
	229.0	6.22	6.19	+03				
	266.5	6.40	6.38	+02				
	283.0	6.46	6.72	-26				
	1445	9.35	9.2	+15				
	1696	10.1	10.1	\pm				
Copper $\theta = 325$; $Q_0 = 120$ kcal; $\frac{m+n+3}{6} = 2.8$	103	10.6	10.4	+2	20.4/80.5	4.0	3.8	+2
	123	12.1	12.1	\pm	82/289	14.0	14.2	-2
	143	13.1	13.1	\pm	289/523	17.4	17.2	+2
	163	13.9	14.4	-5	523/648	18.7	18.6	+1
	183	14.5	14.7	-2	648/773	19.5	19.6	-1
	203	15.0	15.0	\pm				
	223	15.4	15.9	-5				
	243	15.8	16.1	-3				
Gold $\theta = 190$; $Q_0 = 145$ kcal; $\frac{m+n+3}{6} = 3.0$	263	16.0	16.1	-1				
	283	16.3	16.3	\pm				
	103	11.7	11.8	-1	83/290	13.2	13.2	\pm
	123	12.4	12.3	+1	290/373	14.4	14.3	+1
	143	12.8	12.7	+1				
	163	13.1	13.05	+05	323	14.4	14.4	\pm
	183	13.4	13.3	+1	373	14.6	14.6	\pm
	203	13.6	13.7	-1	573	15.5	15.5	\pm
	223	13.75	14.15	-4	773	16.4	16.3	+1
	243	13.9	14.2	-3				
	263	14.0	14.3	-3				
	283	14.1	14.4	-3				
	323	14.4	14.5	-1				

TABLE XIV. - CHARACTERISTIC TEMPERATURES OF SEVERAL ELEMENTS

	Diamond	Platinum	Iridium	Copper	Gold
θ_0 Computed	1860	235	280	325	180
θ Observed	1860	230	283	325	190

TABLE XV. - THERMAL EXPANSION COEFFICIENT OF FLUORITE AND PYRITE

	T	$\frac{1}{l} \frac{\partial l}{\partial T} \times 10^6$		Computed- Observed
		Computed	Observed	
Fluorite (CaF_2) $\theta = 474$; $Q_0 = 309$ kcal; $\frac{m+n+3}{6} = 5.5$	94.4	7.10	7.17	-07
	124.9	10.42	10.26	+16
	157.3	13.09	13.02	+07
	186.9	14.83	14.65	+18
	209.8	15.93	16.04	-11
	231.4	16.80	16.78	+02
	255.6	17.62	17.58	+04
	278.6	18.30	18.53	-23
	313.0	19.22	19.12	+10
Pyrite (FeS_2) $\theta = 645$; $Q_0 = 556$ kcal; $\frac{m+n+3}{6} = 4.65$	108.0	2.88	2.95	-07
	129.7	4.00	3.92	+08
	155.0	5.15	5.16	-01
	214.8	7.22	7.09	+13
	237.4	7.77	7.73	+04
	269.7	8.41	8.43	-02
	313.0	9.10	9.08	+02

TABLE XVI. - EXPANSION COEFFICIENTS OF ZINC AND CADMIUM PARALLEL AND PERPENDICULAR TO THE HORIZONTAL AXES

t_1/t_2 , °C	T_m , abs	$\alpha_{ } \times 10^6$		$\alpha_{\perp} \times 10^6$		$\frac{1}{3} (\alpha_{ } + 2\alpha_{\perp}) \times 10^6$	
		Observed	Computed	Observed	Computed	Observed	Computed
Zinc	333.2 273.2 233.2 193.2 153.2 113.2 53.2	+63.9	----	+14.1	----	+30.7	----
		54.3	+62.5	12.5	+12.0	29.7	+28.8
		55.1	62.8	11.3	11.2	29.2	28.4
		65.4	63.2	10.1	10.1	28.5	27.8
		65.6	63.7	8.3	8.4	27.4	26.8
		64.4	63.9	+5.0	+5.0	24.8	24.6
		52.5	51.2	-2.1	-3.9	16.1	14.5
Cadmium	333.2 273.2 233.2 193.2 153.2 113.2 53.2	+52.6	----	+21.4	----	+31.8	----
		54.3	+57.8	19.1	+16.8	30.3	+30.5
		55.4	57.9	17.8	16.4	30.3	30.2
		56.7	58.1	16.4	15.8	29.9	29.9
		58.0	58.5	14.6	14.6	29.1	29.2
		58.9	58.8	11.7	12.3	27.4	27.8
		54.5	54.3	+3.6	+2.3	20.6	19.6

TABLE XVII. - THERMAL ELASTIC CONSTANTS OF ZINC AND CADMIUM

	$\bar{\theta}_x$	$\bar{\theta}_z$	$\bar{\gamma}_x$	$\bar{\gamma}_z$	$(s_{11} + s_{12}) \times 10^{13}$	$s_{13} \times 10^{13}$	$s_{33} \times 10^{13}$
Zinc	320	300	2.04	1.68	+7.5	-6.05	+28.2
Cadmium	214	200	2.9	2.36	+10.8	-9.3	+35.5

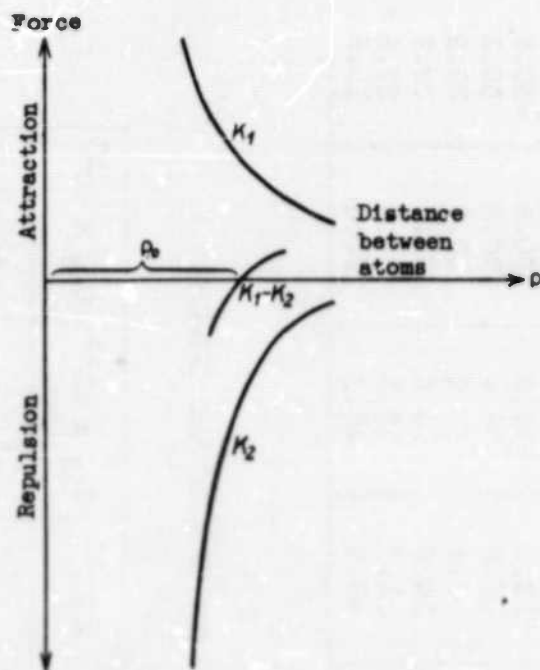


Figure 1. - Superposition of attraction and repulsion.

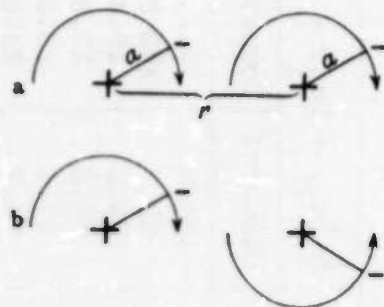


Figure 2. - Sketch to explain cohesion.

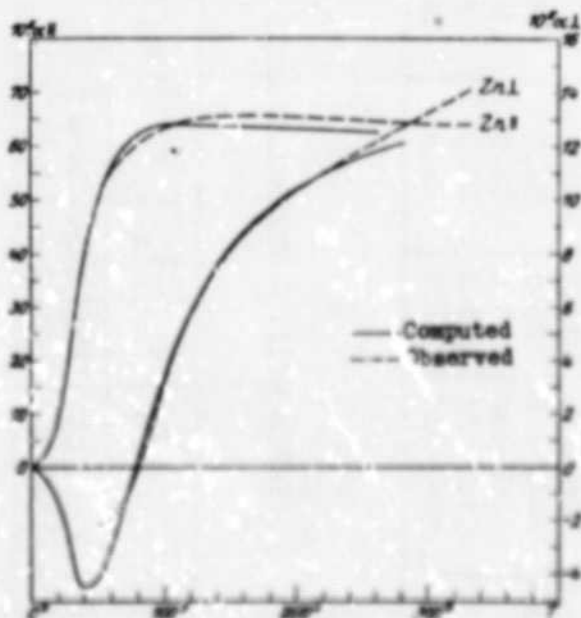


Figure 3. - Principal expansion coefficients of zinc as a function of temperature.

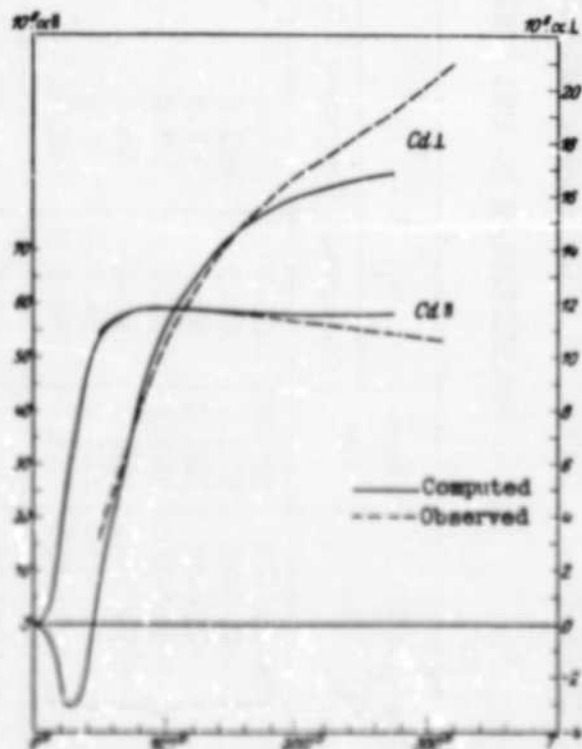


Figure 4. - Principal coefficients of expansion of cadmium as a function of temperature.

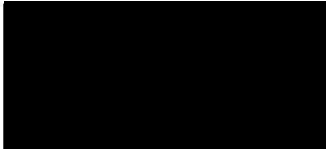
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December 19, 2012

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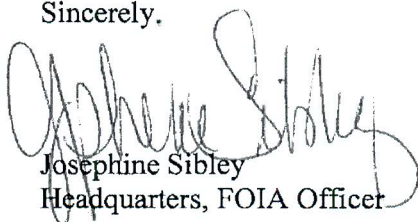
Dear 

Thank you for your Freedom of Information Act (FOIA) request dated and received December 6, 2012, at the NASA Headquarters FOIA Office. Your request was for:

NASA RE 2-18-59W. In is entitled "The State of a Solid Body" by E. Gruneisen, dated 1959. The report is a translation of 1926 German article.

The NASA Headquarters program office(s) conducted a search for Agency records. Attached is the responsive document for your request. Fees for processing this request are less than \$15.00 and are not being charged in accordance with 14 CFR § 1206.700(i)(2). Please call Ms. Josephine Sibley at (202) 358-2462 for further assistance.

Sincerely,


Josephine Sibley
Headquarters, FOIA Officer